
PRINCIPLES OF POLYMER SYSTEMS

Second Edition

FERDINAND RODRIGUEZ
Professor of Chemical Engineering
Cornell University

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PREFACE

In the decade since the first edition appeared, the U.S. polymer industry has shown signs of maturity along with the rest of the economy. Energy conservation and resource management have become essential. Innovations still abound and business is profitable, but the emphasis is on selective areas for growth rather than diversification. Overseas, polymer production increased dramatically in Japan, Germany, and other countries in the early 1970s. Both in the United States and abroad, plastics continue to grow at the rate of 7 to 10% per year, whereas textiles, rubber, and coatings follow more closely the gradual growth pattern of the general economy.

The polymer literature has continued to expand without any sign of reaching a plateau. The last 10 years have seen the publication of hundreds of books on polymers, most of which are included in the General References appended to each chapter. A number of new journals have appeared and are listed in Appendix 3 of this book.

Choosing units for a textbook is not an easy task. The *System Internationale* (SI) has been endorsed by most technical societies and has been accepted by many publications. However, significant areas of industry and academia have been slow to adopt the new units. In this text, SI is emphasized along with parts of the older, largely compatible, cgs system. Masses are given in grams and kilograms and distances in multiples of the meter (not metre, the SI form). Stresses and pressures are in multiples of the pascal (Pa) with other units (dyn/cm^2 , psi) often given as alternatives. The recommended unit for volume, cubic meter, is awkward for many purposes, so cubic centimeter and liter have been used without apology. The convenience of the calorie as a measure of energy is so well embedded in the existing literature that it seems foolhardy to try to replace it completely by the joule for this edition. As a coward's way out, conversion factors are supplied liberally.

Because water has a viscosity of about 1 centipoise at room temperature, most industrial workers continue to use the centipoise or poise as a reference. Perhaps in the near future the millipascal-second ($\text{mPa}\cdot\text{s}$), which is equal to the centipoise,

will achieve acceptance. The term mole as used here is the formula weight of a compound in grams. Concentrations are variously expressed as moles per liter and grams per deciliter (g/dl) where appropriate.

For many decades, chemists and engineers have contended with mixtures of units. Gallons, Btu, horsepower, pounds, and feet still confront us in most reference tables and manufacturers' literature. It is hoped that the use of non-SI units in this book will not offend any reader any more than the omission of some cherished older unit will cause undue strain. Strain, fortunately, is dimensionless. A table of equivalents is included at the end of this preface to supplement the conversion factors and dual scales used in this text.

As with the first edition, I continue to be indebted to students and co-workers for added insights and continued stimulation. Special thanks go to my wife, Ethel, for her encouragement and for her help with typing parts of the manuscript.

Ferdinand Rodriguez

Equivalents for Selected SI Quantities

Quantity	SI unit	Value in cgs units	Value in British units
Mass	kg	1.000×10^3 g	2.200 lb _m
Length	m	1.000×10^2 cm	3.281 ft
Area	m ²	1.000×10^4 cm ²	10.76 ft ²
Volume	m ³	1.000×10^6 cm ³ , or 1.000×10^3 liter	35.31 ft ³ , or 264.2 gal (U.S.)
Force	N (newton)	1.000×10^5 dyn	0.2248 lb _f
Energy	J (joule), N·m	1.000×10^7 erg, or 0.2389 cal	0.7376 ft·lb _f , or 0.9481×10^{-3} Btu
Pressure, stress	Pa (pascal), N/m ²	10.00 dyn	1.450×10^{-4} lb _f /in ² , psi
Viscosity	Pa·s	10.00 P (poise)	6.72 lb _m /ft·s
Power	W (watt), J/s	1.000×10^7 erg/s, or 14.34 cal/min	1.341×10^{-3} hp, or 3.413 Btu/h
Specific heat	J/kg·K	2.389×10^2 cal/g·°C)	2.389×10^2 Btu/lb _m ·°F
Heat transfer coefficient	W/m ² ·K	0.2389 cal/m ² ·s·°C)	0.1761 Btu/ft ² ·h·°F
Impact strength	J/m		1.873×10^{-2} ft·lb _f /in

PREFACE TO THE FIRST EDITION

A man was asked the question, "Do you have trouble making decisions?" He thought a while and then finally answered, "Well, yes and no." The engineer or scientist who is asked to make generalizations about polymers often finds himself in the same position. In the interests of organizing the body of information about polymers which has accumulated since Baekeland, Staudinger, Mark, Carothers, and other pioneers started their work, there is a tendency to overgeneralize. The road of polymer discovery is strewn with the bones of absolute statements. In the older literature one finds such pronouncements as, "All polymer crystals are submicroscopic," "Five-membered rings are too stable to be opened to form linear polymers," "Maleic anhydride cannot be homopolymerized," and "Stereoregular polymers can be made only with an optically active catalyst." All of these have been disproved or qualified. In this book, any generalizations that are encountered are subject to the following *caveat*: "All generalizations are partially untrue, except this one."

It has been the author's aim in this book to relate the behavior of polymer systems whenever possible to examples that are part of everyday experience. With polymers the job should be simple, since many of the things we use—our clothing, our food, and our bodies—are made up of polymer systems.

It scarcely needs saying that this introductory text cannot treat any one subject exhaustively and must, perforce, omit some. However, the student who wants to learn more about polymers easily can, like Leacock's distraught young lord, jump on his horse and ride wildly off in all directions. Not only are there many journals devoted to polymers, the journals themselves divide and grow in yeasty fashion. Journals devoted to reviews of selected topics in polymers have made their appearance along with a flood of monographs. The list in Appendix 3 includes many of the English-language sources. The futility of trying to present a complete picture of polymer systems in one text is best illustrated by reference to the massive "Encyclopedia of Polymer Science and Technology" (Interscience) which began to be published in 1964.

Despite the great leaps forward made in the last several decades toward understanding polymers, frontiers remain. The mechanisms of flame retarding by halogens and phosphates, drag reduction by dilute polymer solutions, filler reinforcement of rubber and plastics, and the freeze-thaw stabilization of human blood are incompletely understood. Significantly, in each case, the polymer does not have an isolated existence, but is part of a *system*. Perhaps the most challenging frontier of all involves the human system. The use of polymers to stabilize whole blood during extended storage at liquid nitrogen temperatures is but one example of the way in which polymer systems can be applied in the interests of humanity.

I gratefully acknowledge the permissions granted by journals and industrial firms to reproduce material originally appearing in their publications. Extensive comments on the original manuscript by Professor M. C. Williams of the University of California at Berkeley were very helpful. The assistance and encouragement from students, fellow teachers, and co-workers in industry have been important in making this book possible. I want to thank Professor Charles C. Winding especially for his constructive and friendly guidance. And, of course, I thank my wife and family for the understanding and patience they have shown at all times, but most conspicuously during the writing of this book.

Ferdinand Rodriguez

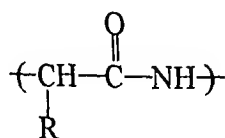
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INTRODUCTION

1-1 POLYMERS

The term *polymer* denotes a molecule made up by the repetition of some simpler unit, the *mer* or *monomer*. It is almost impossible to define the term further to include the many species with which we shall deal and yet to exclude metals, ceramics, and crystalline forms of smaller molecules. In the broadest sense, these are polymers too.

The term *macromolecule*, big molecule, also is used. Large molecules of complex structure can be covered better by this name than by the name "polymer," since the latter carries with it the connotation of a simple repeating unit. An example of a naturally occurring macromolecule is insulin, a protein hormone that occurs in the pancreas. It is best known as an agent to lower blood sugar in diabetic patients. The structure has repeating units with amide linkages:



A macromolecule of insulin has a total of 51 such units with 16 variations of R. Proteins, nucleic acids (DNA, RNA), and enzymes generally are complex macromolecules. On the other hand, some naturally occurring polymers have a simple repeating unit. Starch, cellulose, and natural rubber are examples of polymers which are chains of a simple unit repeated thousands of times. Cellulose, in the form of cotton, is useful as a textile fiber without chemical modification. The polymer-based industries all started with such naturally occurring materials. A second stage in industrial development has been the modification of a natural polymer to make it more useful. All industries have found that entirely synthetic polymers, built up from small molecules such as ethylene and propylene, offer the broadest spectrum of properties. Obviously,

the natural materials have a firm place in technology. However, when the idea arises of "tailoring" a polymer to certain end use requirements, the wholly synthetic polymers often provide an economical solution.

1-2 POLYMER-BASED INDUSTRIES

Until the 1920s and 1930s, the several industries that depend on polymeric materials grew rather independently of one another and were based on natural or modified-natural materials. These industries can be identified in the broad sense as

Rubber

Plastics

Fibers

Coatings

Adhesives

In fact, it was not until after World War II that the dividing lines became so blurred as to make it difficult to classify some companies.

Rubber

Even in pre-Columbian times, the natives of South and Central America made use of the latex obtained by puncturing the bark of certain trees. By coagulating the latex, a rubber ball could be produced that was used in the national sport of the Mayan Indians. MacIntosh and Hancock in England and Goodyear in the United States (1839) discovered that mixing natural rubber with sulfur gave a moldable composition that could be heated (vulcanized) and converted to a useful, nontacky, stable material suitable for raincoats, waterproof boots, and solid tires for carriages. The general progress of the rubber industry soon became associated with the automobile. Even today, about 70 percent of all types of rubber ends up in tires and a good part of the remainder is used in gaskets, grommets, and other parts of the modern auto. The pneumatic tire (Dunlop, 1888) and the use of carbon black as a reinforcing filler and of organic accelerators for the sulfur cross-linking reactions were achieved with natural rubber. Since World War I, most natural rubber has been cultivated in Malaysia and Indonesia rather than the Americas. Between World Wars I and II the development of synthetic rubbers was pursued, especially in Germany and the United States. In Germany, emphasis was on general-purpose rubber to reduce dependence on far-flung sources of supply. In the United States, more emphasis was placed on specialty rubbers, such as Thiokol rubber and neoprene, which would be more resistant to swelling by solvents than natural rubber. During World War II, Germany and Russia had developed synthetic rubbers so as to be self-sufficient. In the United States, a crash program was instituted that was to affect all other polymer-based industries eventually. Production of a styrene-butadiene copolymer (GR-S, later called SBR) went from zero in 1941 to over 700×10^6 kg in 1945. In Fig. 1-1, the drop in natural rubber consumption and the development of SBR rubber during World War II (1941 to 1946) can be seen. Despite a brief resurgence of interest in natural rubber after the war, the synthetic material has gained consistently. The primary results of the SBR program were:

1. Tremendous production capacity for styrene and butadiene monomers
2. Independence of American industry from rubber imports for many uses
3. Availability of synthetic rubber latex for other uses
4. New insight into polymer production and characterization

Not the least of the accomplishments was the overnight conversion of many scientists and engineers into polymer engineers, polymer chemists, polymer physicists,

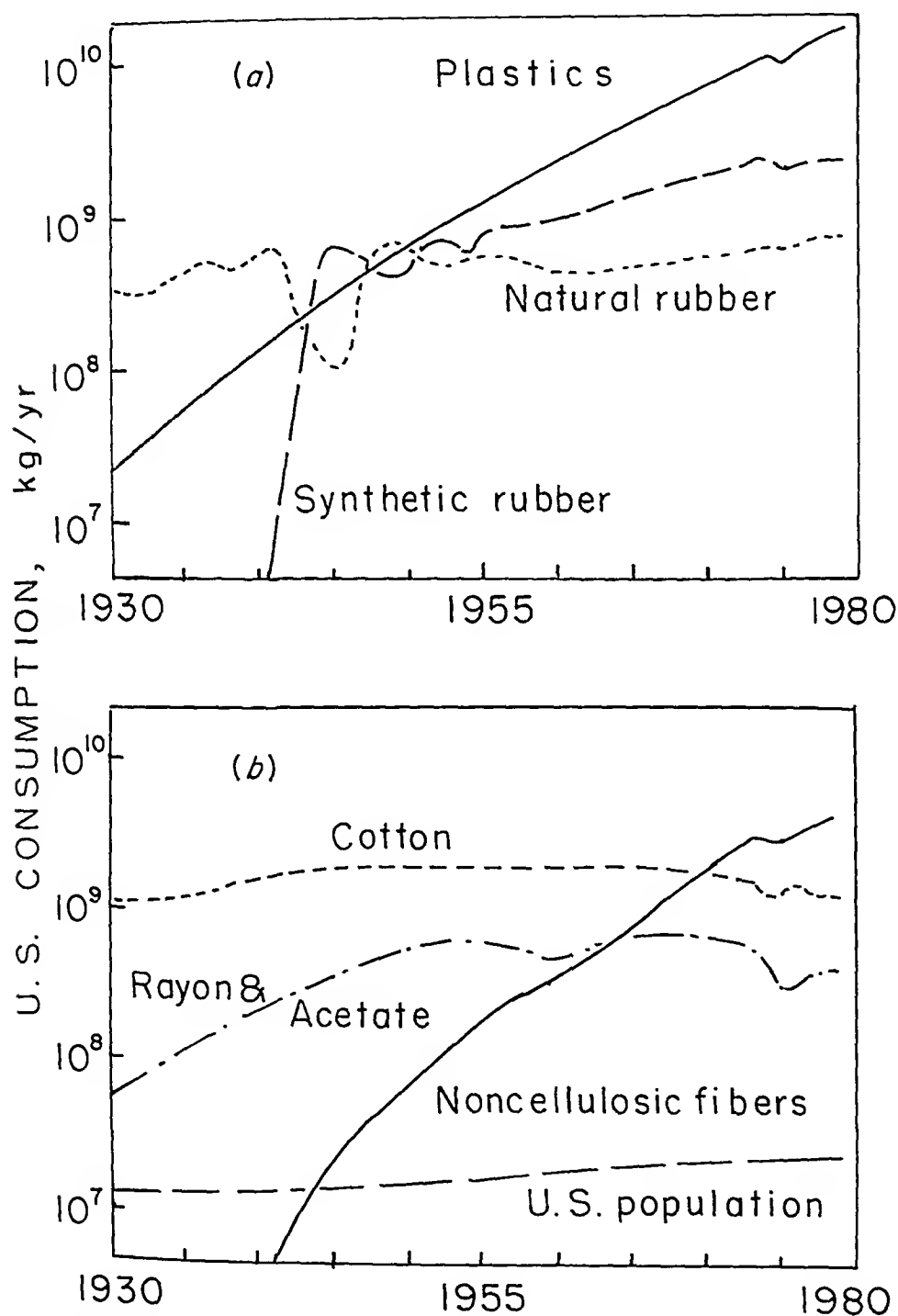


FIGURE 1-1

Polymer consumption can be compared with the gradual growth of the population of the United States, which was estimated to be 2.3×10^8 in 1979: (a) plastics and rubber; (b) fibers.

etc. After the war, their interest remained in the field, so that the rather thin prewar ranks of textile, rubber, paint, etc., researchers were suddenly swelled by large numbers of highly trained people who were not wedded to any one industrial viewpoint. The exchange of technology between industries that now is quite common can be credited in great measure to the proper recognition of the principles of polymer science and technology as the underlying basis for all these fields.

During the 1970s, consumption of rubber in the United States leveled off and the ratio of synthetic to natural rubber did not change much (Table 1-1). Various factors contributed to this phenomenon. The trends to smaller automobiles, lower speed limits, and higher-priced fuel all softened the demand for rubber in transportation. Moreover, the change in construction of tires has had several effects. Belted-radial tires use a higher ratio of natural rubber and *cis*-polybutadiene to SBR than the older bias-ply tires. The radial tires often wear longer, which helps to make up for their higher initial cost. The net result is a decreased demand for replacement tires. In the 1950s, a life of 20,000 mi (32,000 km) was considered acceptable for a bias-ply tire. Many radial tires now can be expected to last twice as long.

In Table 1-2, the change in usage of polymers in the three major categories is summarized for the decade 1968 to 1978. The overall demand for rubber has not increased nearly as much as the demand for fibers and plastics. Another feature of the 1970s as opposed to the 1950s is the increased competition among synthetic materials. The old rivalry between natural rubber and SBR culminated in a rather constant ratio of usage. In the 1980s a continuing rivalry for many markets pits the thermoplastic elastomers against the older vulcanizable (cross-linkable) rubbers such as SBR, neoprene, butyl, and nitrile.

Plastics

During Civil War days, daguerreotype cases were molded out of compositions containing shellac, gutta-percha, or other natural resins along with fibrous materials. The compression molding machinery and dies that were used were quite similar in principle to those used a hundred years later. Hyatt's discovery (1868) that nitrated cellulose mixed with camphor could be molded under pressure to give a hard, attractive material

TABLE 1-1
Rubber Consumption in the United States* (in units
of 10^9 kg)

Year	All synthetics	SBR	Natural
1970	1.9	1.2	0.60
1971	2.1	1.4	0.58
1972	2.3	1.4	0.64
1973	2.4	1.5	0.69
1974	2.3	1.4	0.72
1975	1.9	1.1	0.65
1976	2.3	1.3	0.67
1977	2.5	1.4	0.78
1978	2.4	1.4	0.78

*Source: U.S. Dept. of Commerce.

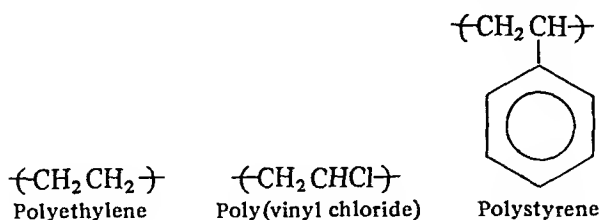
TABLE 1-2
Polymer Consumption in the United States* (in units of 10⁶ kg)

	1968	1978
Plastics (sales)	6,870	16,124
Thermosets	1,423	3,037
Alkyd	150	215
Epoxy	70	143
Phenolic	408	700
Polyester (unsaturated)	244	549
Polyurethane foams	277	840
Urea and melamine	274	590
Thermoplastics	5,447	13,087
Acrylic	145	253
Cellulosics	87	74
Nylon	33	126
Polycarbonate	12	95
Polyester (saturated)	—	280
Polyethylene (high density)	545	1,893
Polyethylene (low density)	1,364	3,249
Polypropylene	377	1,389
Polystyrene and other styrenics	1,416	2,741
Poly(vinyl chloride)	1,095	2,641
Others	373	346
Rubber (production figures)	3,149	3,234
Natural rubber (consumption)	593	779
Styrene-butadiene	1,488	1,377
Polybutadiene	327	379
Neoprene	(with "other")	160
Ethylene-propylene	116	174
Butyl	154	152
Nitrile	82	72
Other	389	141
Fibers (consumption figures)	4,400	5,677
Natural and mineral	2,240	1,769
Cotton	1,885	1,287
Wool	172	60
Glass	183	422
Synthetic organic fibers	2,160	3,908
Rayon	548	253
Cellulose acetate	220	137
Nylon	578	1,156
Polyester	459	1,722
Acrylic	233	328
Polyolefin	122	312

*Source: U.S. Dept. of Commerce.

suitable for billiard balls and detachable collars is often cited as the start of the plastics industry. Others date it from 1907, when Baekeland patented a wholly synthetic material based on the reaction of phenol and formaldehyde. The industry has expanded continuously with scarcely a pause in 50 years (Fig. 1-1). The capacity for styrene production as a result of the synthetic rubber program after World War II was

an important factor. The need for polyethylene and poly(vinyl chloride) during the war also accelerated industrial know-how. By 1960, each of these three polymers was being produced at the rate of over a billion pounds per year.



The development of new materials and fabricating techniques has filled the gap between plastics and rubber. However, at present, the distinction is still a useful one.

Increased production and keen competition, especially among the producers of the billion pounds per year of plastics and synthetic rubber, kept the prices of polymers from increasing from 1950 to 1974, despite the inflationary pressures of the general economy. In fact, the average price of plastics and resins decreased. The Wholesale Price Index plotted in Fig. 1-2 is the Industrial Commodity Index. The price pattern for butyl rubber (Fig. 1-2) is typical of that for synthetic rubbers in general, showing almost no change until the 1970s. Natural rubber, on the other hand, is traded on the international commodity market and is sensitive to political as well as economic factors.

The year 1974 brought a dramatic change in polymer pricing. The embargo on

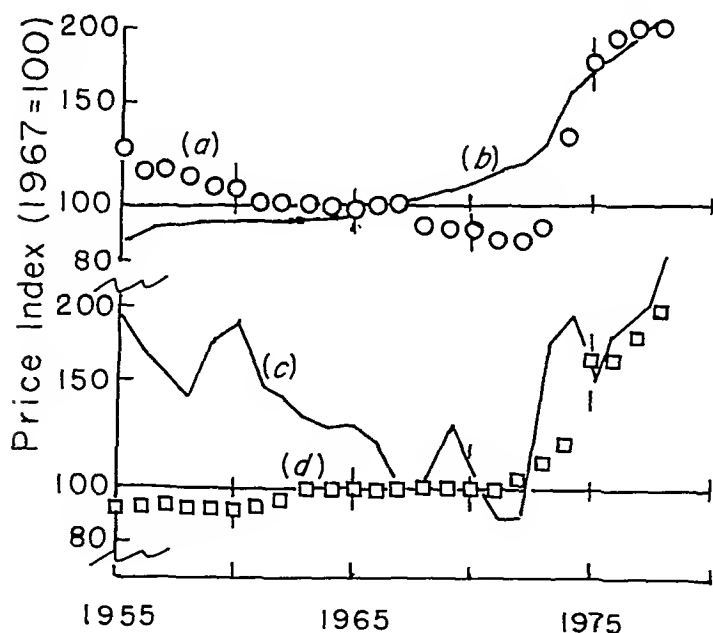


FIGURE 1-2

The Wholesale Price Indexes (U.S. Dept. of Commerce) for (a) plastics and resins, (b) industrial commodities, and (c) natural rubber. Relative prices for (d) butyl rubber are taken from manufacturer's literature. The base year for the indexes is 1967.

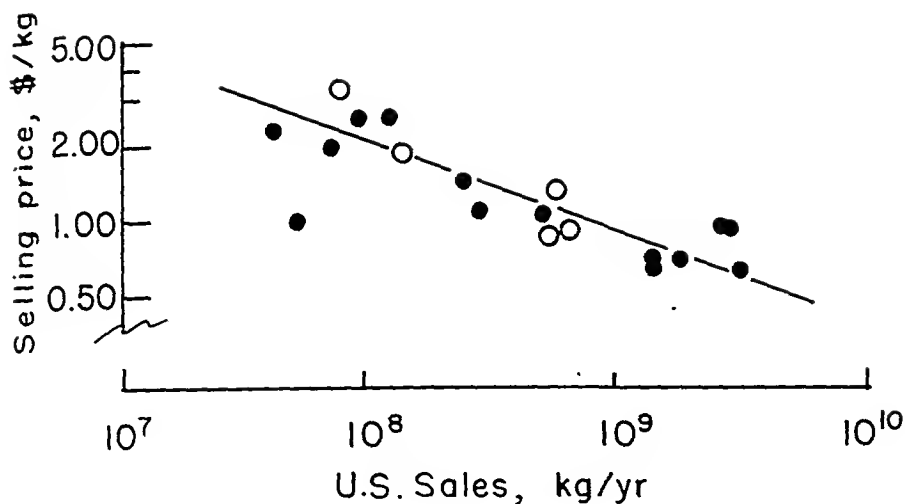


FIGURE 1-3

Prices of general-purpose-grade thermoplastics (●) and thermosets (○). Data for 1979 taken from *Modern Plastics*, January 1980. The line is drawn with a slope of -0.4 .

imported oil in that year had a number of consequences, one of which was a temporary shortage of most polymers. While all commodities reflected the general inflation rate (Fig. 1-2), the price of plastics increased sharply. A drop in polymer consumption the following year (seen in Figs. 1-1 and 1-2) led to some price reductions, but the old pattern of a decreasing price trend that had prevailed for over 25 years after World War II has not reappeared. In fact, 1978 and 1979 again saw sharp increases, although this perhaps only reflected the generally increased inflation rate for all commodities in the United States. As a point of reference, in the base year 1967, the price of natural rubber was \$0.20/lb (\$0.09/kg); butyl rubber, \$0.25/lb (\$0.11/kg); and the average price of plastics and resins was about \$0.22/lb (\$0.10/kg).

Other commodities also have been affected by inflation, even when they are not directly derived from petroleum. Some items can be compared on the basis of their price indexes as of 1978 (where 1967 is the base year for a price index of 100):

Consumer prices	195.4
Industrial commodities	209.4
Plastics and resins	199.8
Iron and steel	253.6
Lumber	322.4
Wood pulp	266.4
Paper	206.1
Glass containers	244.4
Crude rubber	187.2

The last item includes both natural and synthetic rubber.

It is to be expected that increased volume for any manufactured product would lead to economies of scale. This is the case, although there is no firm rule that applies. When a large number of diverse polymers are compared (Fig. 1-3), there is a discernible trend which can be expressed as

$$\text{Selling price} = k_a(\text{production scale})^{-a} \quad (1-1)$$

where a is between 0.1 and 0.4 and k_a increases from year to year. A widely used rule of thumb is that the cost of equipment increases with the production capacity to the 0.6 power. If all other factors follow the same trend, then, obviously, the cost of production would, indeed, decrease with the -0.4 power.

Another way of looking at prices is by a "learning" or "experience" curve. If price is plotted against time or against cumulative production volume, there should be a gradual decrease reflecting economies from debottlenecking, incremental increases in capacity with small investment, and, eventually, lowered plant depreciation. Even if volume per unit time remains constant, experience should lower price. Unfortunately, inflation causes the "baseline" of such a plot to drift, and attempts to correct for this (to plot in "constant" dollars) involve many assumptions.

Fibers

The shift from natural polymers to modified-natural and then to wholly synthetic is still underway in the fibers industry. Regenerated cellulose (rayon) and cellulose acetate were introduced around the turn of the century, and nylon was the only wholly synthetic fiber produced in quantity before World War II. In the decade from 1968 to 1978, cotton and wool production decreased while polyester and nylon fiber production boomed. During the same period, rayon and cellulose acetate also diminished in importance (Fig. 1-1, Table 1-2). Pollution problems inherent in rayon manufacture caused some plants to close down in the 1970s. A factor favoring synthetic fibers has been the fashion trend to "easy-care" fabrics and garments. Cotton and wool require chemical treatment to compete on this basis. Synthetic fibers also have had a price advantage in recent years due partly to labor costs. Cotton and wool are "labor-intensive" materials compared to the synthetics.

Coatings

Decorative and protective coatings have been based on unsaturated oils (linseed oil, tung oil) and natural resins (shellac, kuari gum) for centuries. In the 1930s synthetic resins (alkyd resins), which really are modified natural oils, became important. The SBR rubber program had its repercussions in the coatings industry, since styrene-butadiene latexes were found to be useful film-formers. Latex paints based on vinyl acetate and acrylic resins now have been developed for outdoor as well as indoor applications. Such water-thinnable coatings represent most of the interior coatings and about half the exterior paints for houses. In 1979, total sales of coatings amounted to about \$4 billion, about equally divided between trade sales (directly to consumers) and industrial finishes (to manufacturers of other products such as automobiles, appliances, etc.). Legislation in most states now limits the solvents that can be used in commercial coating applications, both in type and in amount. Water-thinned and powdered coatings have been substituted for solvent-based paints and lacquers in some instances.

Adhesives

Since adhesives often must be specifically designed to bond to two different surfaces, an even greater diversity of products has been developed than in coatings. In similar

fashion to the coatings industry, the adhesives industry has made use of the latex technology developed in World War II. Many natural polymers are still used, but almost every new plastic and rubber developed has spawned a counterpart adhesive. The development of the highly advertised “super glues” based on the cyanoacrylates (see Sec. 12-4, Adhesives) was atypical in that the materials were used as adhesives first and not adapted from some prior application as plastics or coatings.

1-3 FEEDSTOCKS FOR POLYMERS

Even when considered only as the monomer for the homopolymer, ethylene is a very important commodity. More than that, it is an essential ingredient in vinyl chloride and styrene, the other two largest volume monomers for plastics (Fig. 1-4). Polymer-grade propylene and butadiene are made in large measure as by-products of ethylene manufacture. As seen in Fig. 1-4, these two raw materials enter into the production of virtually all the other major plastic, rubber, and fiber polymers. Since polyethylene accounted for about one-third of the 17.6×10^9 kg of plastics produced in 1979, it is reasonable that the production of ethylene parallels rather closely the production of polymers in general, and of polyethylene in particular (Fig. 1-5). Although the recession of 1975 set growth back by about three years, the growth rate has been about 11 percent per year for the period 1975 to 1979.

Building a new ethylene-producing plant is no small undertaking. A facility for producing 500×10^6 kg/year cost at least \$100 million in 1979. Ethylene can be made from a variety of starting materials. Ethane recovered from natural gas is a “clean” feed, in that few by-products occur (Table 1-3). Natural gas is a diminishing resource, so almost all new plants are made to use heavier feeds such as heavy naphtha (boiling range of 100 to 220°C) or atmospheric gas oil, AGO (boiling range of 200 to 350°C). Almost any other hydrocarbon source is a possible feed, but matters of aromaticity and sulfur content change the desirability from one refinery stream to another. The heavier feeds (Table 1-3) yield a greater variety of by-products that must be sold or used to make the process economical. Some chemical companies have been exploring the direct production of ethylene from crude oil, by-passing the usual oil refinery. By recycling various streams, the yield of ethylene can be optimized without having to market gasoline or fuel oil in competition with the traditional oil refiners. No full-scale plants have yet been built using a crude oil feed. The product distribution can differ from that listed in Table 1-3 for various reasons. High *severity* operation may involve higher temperatures and longer residence times during cracking, which increases conversion per pass. Moderate severity operation usually produces more by-products but lessens the amount of feed wasted in less salable materials such as coke.

With any feed, the hydrocarbon source mixed with steam is pyrolyzed at 850°C or higher for up to 1 s by passage through a tube set in a *cracking* furnace. The steam is added to decrease formation of coke on the tube walls. The hot effluent gases are *quenched* with water or oil to stop the reaction. Separations using distillation and absorption are used to obtain pure products as well as to recycle some materials. The relative merits of various feed stocks and cracking processes have been the topics of numerous journal articles.

A review of the production and economics of ethylene, propylene, and butadiene

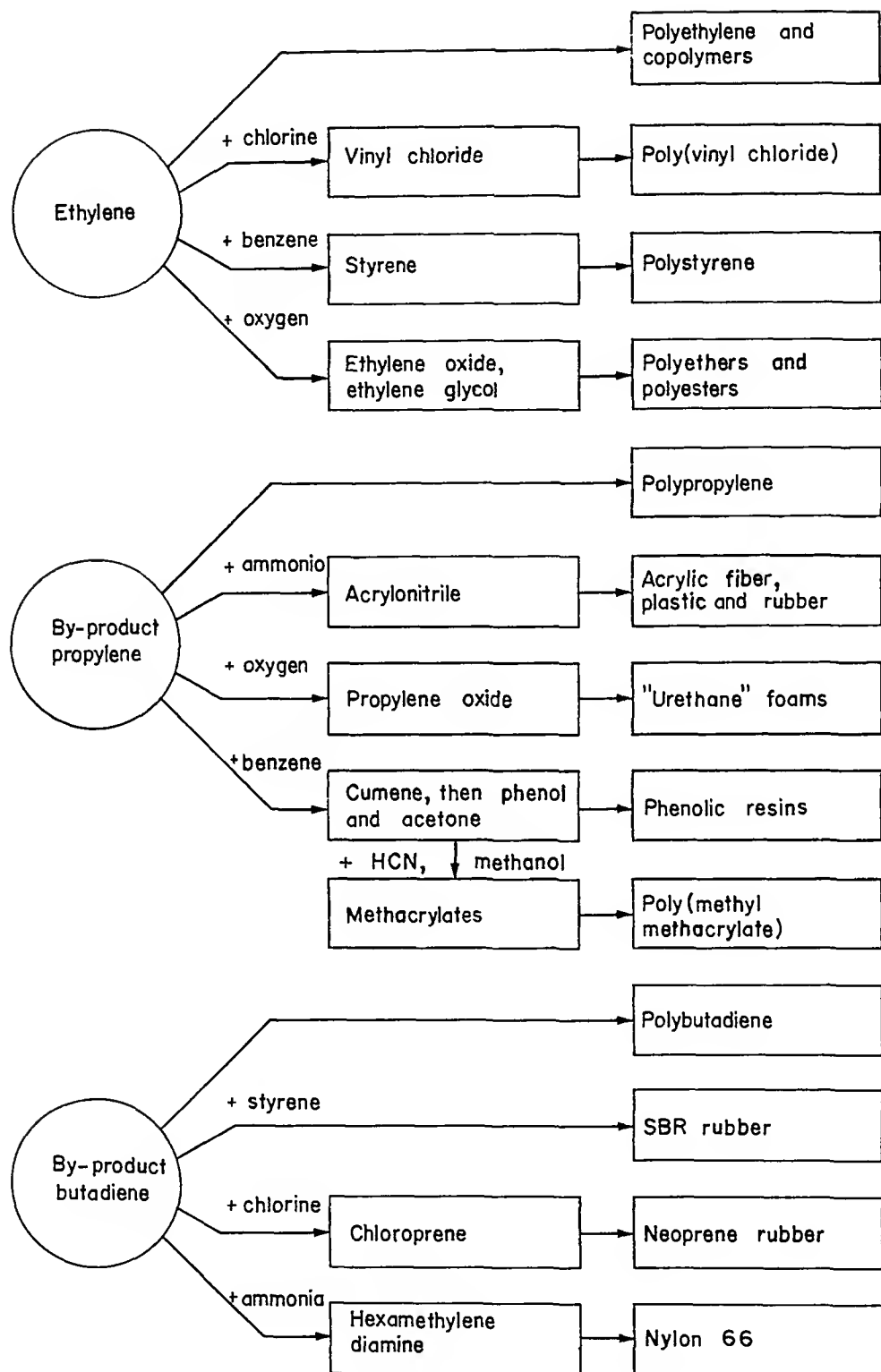


FIGURE 1-4

Major polymeric products derived from ethylene and its by-products. Not all reactants or products are shown.

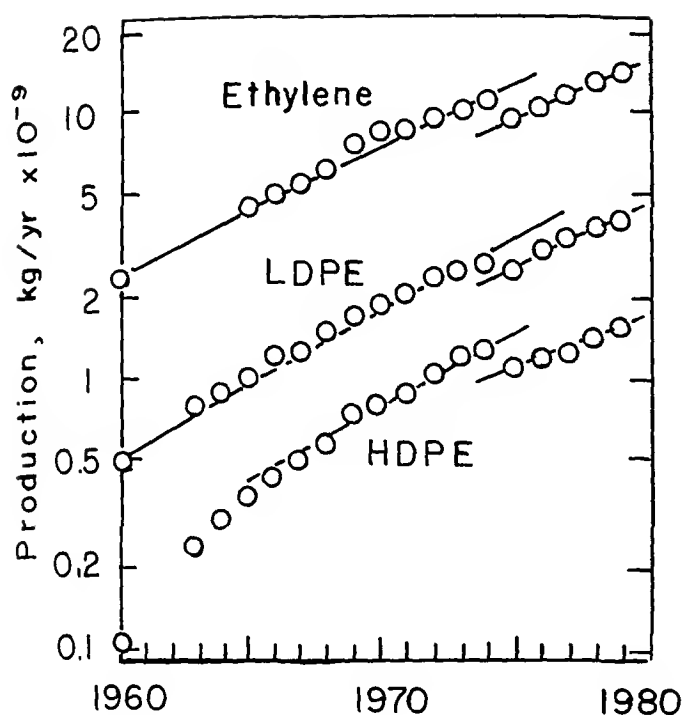


FIGURE 1-5

Production rates of ethylene and polyethylene (low-density and high-density).

appears in *Chemical and Engineering News* once each year, usually in November. Vinyl chloride and styrene as well as other chemicals are also reviewed annually. As a measure of energy usage in the United States, it may be pointed out that the entire synthetic polymer industry (plastics, rubber, and fibers) produced about 22 billion kg in 1978 while almost 10 times that weight of hydrocarbon was burned as fuel in passenger automobiles.

TABLE 1-3

Typical Product Profile for Production of 1000 Parts by Weight of Ethylene from Various Feedstocks*

Product	Feedstock				
	Ethane	Propane	Naphtha	Atm. gas oil	Crude oil
Ethylene	1000	1000	1000	1000	1000
Acetylene	—	—	—	—	200
Propylene	24	375	420	557	135
Butadiene	30	69	141	187	90
Other C ₄ 's and gasoline	24	158	848	1019	435
Fuel oil	—	—	195	729	600
Residue gases	172	659	521	457	—
Pitch	—	—	—	—	583
Total feed	1253	2260	3126	3951	3050

* After S. C. Stinson, *Chem. Eng. News*, 57:32 (May 28, 1979).

TABLE 1-4
A Selected Chronology of Polymer Technology

1770	Priestley gives rubber its name because it can erase marks on paper
1839	Goodyear (U.S.), MacIntosh and Hancock (England), vulcanization (cross-linking) of natural rubber
1860s	Molding of natural plastics such as shellac and gutta-percha
1868	Hyatt (U.S.), celluloid (cellulose nitrate molded articles)
1891	Chardonnet (France), regenerated cellulose via nitrate
1893 to 1898	Cross, Bevan, Beadle, Stearn (England), viscose rayon fibers
1907	Baekeland (U.S.), phenol-formaldehyde resins
1910	First rayon plant in United States
World War I	Cellulose acetate solutions ("dope") for aircraft; laminated plywood and fabric construction for aircraft fuselages
1920s	Cellulose nitrate lacquers for autos
1924	Cellulose acetate fibers
1926	Alkyd resins from drying oils for coatings
1927	Poly(vinyl chloride) Cellulose acetate plastics
1929	Polysulfide (Thiokol) rubber Urea-formaldehyde resins
1931	Poly(methyl methacrylate) plastics Neoprene (Duprene) synthetic rubber
1936	Poly(vinyl acetate) and poly(vinyl butyral) for laminated safety glass
1937	Polystyrene Styrene-butadiene (Buna S) and acrylonitrile-butadiene (Buna N) rubbers (Germany)
1938	Nylon 66 fibers
1939	Melamine-formaldehyde resins Poly(vinylidene chloride)
1940	Butyl rubber (U.S.)
1941	Polyethylene production (England)
1942	Unsaturated polyesters for laminates
World War II	Silicones, fluorocarbon resins, polyurethanes (Germany), styrene-butadiene rubber in United States, latex-based paints
1947	Epoxy resins
1948	ABS polymers
1950	Polyester fibers
1948 to 1950	Acrylic fibers
1954	Polyurethane foams in United States
1956	Linear polyethylene, acetals [poly(oxymethylene)]
1957	Polypropylene, polycarbonates
1959	Chlorinated polyether Synthetic <i>cis</i> -polyisoprene and <i>cis</i> -polybutadiene rubbers
1960	Ethylene-propylene rubber Spandex fibers
1962	Phenoxy resins, polyimide resins
1965	Poly(phenylene oxide), polysulfones, styrene-butadiene block copolymers
1960s	Cyanoacrylate adhesives Aromatic polyamides, polyimides Silane coupling agents
1970	Polybutene (isotactic)
1971	Poly(butyl terephthalate)
1970s	Thermoplastic elastomers based on copolyesters Poly(phenylene sulfide)
1977	Polynorbornene (rubber)

1-4 POLYMER SCIENCE

The chemistry and physics of polymers lagged behind technology for many years. In 1920, Staudinger proposed his macromolecular hypothesis, saying that substances like natural rubber were not colloidal, physical associations of small molecules but were truly long-chain molecules of extremely high molecular weight. Since such materials were not easily characterized by the methods used with small molecules, most chemists regarded polymer research as a rather undignified occupation. However, the studies of Emil Fischer on proteins, Meyer and Mark on cellulose, and Carothers on polycondensation had established a basis for acceptance of Staudinger's ideas by the 1930s. Once again, World War II must be recognized as a time when research accelerated sharply and theories started to catch up with practice. Debye's work on light scattering, Flory's on viscous flow (as well as other areas), and Harkins' on a theory of emulsion polymerization grew out of government-sponsored projects. The discovery by Ziegler of synthetic catalysts that would give ordered polymers and the extension of such systems by Natta in the 1950s changed many fundamental ideas of polymer science, as did the discovery of large single crystals of high polymers a few years later.

Capsule chronologies of polymer technology and science are given in Tables 1-4 and 1-5.

TABLE 1-5
A Selected Chronology of Polymer Science

1806	Gough (England) experiments with elasticity of natural rubber
1838	Regnault (France) polymerizes vinylidene chloride via sunlight
1859	Joule (England) demonstrates thermodynamic principles of elasticity of rubber
1884 to 1919	Emil Fischer (Germany) establishes formulas of many sugars and proteins
1920	Staudinger (Germany) advances macromolecular hypothesis
1928	Meyer and Mark (Germany) measure crystallite sizes in cellulose and rubber
1929	Carothers (U.S.) synthesizes and characterizes condensation polymers
1930 to 1934	Kuhn, Guth, and Mark (Germany) derive mathematical models for polymer configurations; theory of rubber elasticity
World War II	Debye, light scattering of polymer solutions; Flory, viscosity of polymer solutions; Harkins, theory of emulsion polymerization; Weissenberg, normal stresses in polymer flow
1950s	Ziegler, coordination complex polymerization; Natta, tacticity in polymers; Swarc, living polymers; interfacial polycondensation
1955	Williams-Landel-Ferry equation for time-temperature superposition of mechanical properties
1957	Single crystals of polyethylene characterized, Keller, Till
1960	T. Smith, the failure envelope
1960s	NMR applied to polymer structure analysis Orthogonal rheometer, Maxwell GPC analysis for mol. wt. distribution, Moore Differential scanning calorimetry Polybenzimidazoles, Marvel Torsional braid analysis, Gilham
1970s	Interpenetrating networks High-performance liquid chromatography

1-5 FUTURE TRENDS

The only safe generalization is that the polymer industry will continue to grow faster than the general economy and that it will be increasingly dependent on wholly synthetic materials. It is somewhat more risky to say that the consumption of plastics will have to level off in the next 25 years, because extrapolations of current trends would lead to a per capita consumption of 500 kg/year of plastics by the year 2000! On the other hand, the increased use of plastics in automobiles and houses might make even that figure credible. Another aspect of polymer science and technology is the increasing control of chemical structure in polymers. This could lead to entirely new applications, especially in the fields of biology and medicine.

PROBLEMS

- 1-1. What are some large-scale uses of plastics and rubber in the home construction industry that are obvious to the layman?
- 1-2. What are some obvious uses of rubber and plastics in the automobile (in addition to tires)?
- 1-3. What are some drawbacks of ordinary cellulose-based paper for books and newspapers compared with what might be expected from a material based on polyethylene? What disadvantages might the plastic have (in addition to the initial one of price)? What is the potential market for "synthetic" newsprint?
- 1-4. If every one of the 10 million or so automobiles produced in the United States in a single year suddenly were equipped with a thermoplastic polycarbonate windshield, what new selling price might be expected for the general-purpose material?
- 1-5. What factors other than volume produced will affect the selling price of a polymer?
- 1-6. When plastics are used for a molded article, a specified volume of material must be used to achieve a certain effect. However, prices for plastics usually are given on a unit weight basis. If acetal resin is to compete on a cost per volume basis with polypropylene in a given application, what must the price ratio be on a weight basis (see Table A5-1)?
- 1-7. The price of the polymer is only one factor in the selling price of a finished article. Some other items might include other ingredients, production labor, decorating, packaging, and distribution. Rank the following items in the order of increased dependence on polymer cost:

polyethylene garbage can
 nylon panty hose
 nylon guitar string

tinted cellulose acetate sunglasses
 nylon pocket comb
 automobile tire

What factors are important for each item?

- 1-8. Using data from any recent issue of *Chemical Marketing Reporter* (Schnell Publishing Co.), plot the lowest polymer price listed versus monomer price for ethylene, propylene, styrene, vinyl chloride, and bisphenol A (polycarbonate). Should the ratio of polymer to monomer price increase or decrease with monomer price? Why?

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2

BASIC STRUCTURES OF POLYMERS

2-1 CLASSIFICATION SCHEMES

The study of any subject as vast and complex as polymers is simplified by gathering together the many thousands of examples that are known into a few categories about which generalized statements can be made. By speaking about polymers as a special topic, we already are categorizing materials as low-molecular-weight or as high-molecular-weight, i.e., polymers. However, some more useful classifications are by:

1. *Structure.* We can ask whether the polymer exists as a mass of separable, individual molecules or as a macroscopic network. Also, is it branched or linear? Is it a succession of randomly oriented units or does it have some preferred spatial orientation? We shall pursue this approach later in this chapter.
2. *Physical state.* Polymer molecules may be partially crystalline or completely disordered. The disordered state may be glassy and brittle, or it may be molten with the viscosity characteristic of a liquid or the elasticity we associate with a rubbery solid. We shall see that the distinctions depend on temperature, molecular weight, and chemical structure.
3. *Reaction to environment.* Within an industry, or within some other grouping, there may be an important difference in processing or end use behavior. In any application one can differentiate between low-cost, general-purpose materials and high-cost, specialty materials. For engineers this is a very logical categorization as a first step to specifying a material for a given use.

In the plastics industry an important factor in economic usage and in end use stability of a product is the behavior of the material at high temperatures. The term *thermoplastic* is applied to materials that soften and flow upon application of pressure and heat. Thus, most thermoplastic materials can be remolded many times, although chemical degradation may eventually limit the number of molding cycles. The obvious advantage is that a piece that is rejected or broken after molding can

be ground up and remolded. The disadvantage is that there is a limiting temperature for the material in use above which it cannot be used as a structural element. The *deflection* temperature, formerly termed the *heat-distortion* temperature, is measured by a standard loading at a standard rate of temperature rise.

The term *thermoset* is applied to materials that, once heated, react irreversibly so that subsequent applications of heat and pressure do not cause them to soften and flow. In this case, a rejected or scrapped piece cannot be ground up and remolded. On the other hand, the limiting upper temperature in use often is considerably higher than the molding temperature. Once again, chemical stability becomes a limiting factor.

4. *Chemical*. The elemental composition of a polymer, the chemical groups present (ether, ester, hydroxyl, etc.), or the manner of synthesis (chain propagation, transesterification, ring opening, etc.) may be used as a means of classifying polymers. A person or company attempting to exploit a unique raw material or process may profitably use such an approach.
5. *End use*. As has been mentioned before, the various polymer-consuming industries tend to think of a new material as an adhesive, a fiber, a rubber, a plastic, or a coating, even though the material may be adaptable to all these applications.

2-2 BONDING

Polymers generally are held together as large molecules by covalent bonds, while the separate molecules, or segments of the same molecule, are attracted to each other by "intermolecular forces," also termed "secondary" or "van der Waals" forces. Although ionic and other types of bonds can occur in polymeric systems, they are not considered here. Covalent bonds are characterized by high energies (35 to 150 kcal/mol), short interatomic distances (0.11 to 0.16 nm), and relatively constant angles between successive bonds. Some important examples are given in Table 2-1. An apparent exception is the Si—O—Si bond, for which values from 104 to 180° have been reported. The flexibility of this bond, coupled with the ability of methyl groups attached to silicon to rotate about the Si—C bond, is responsible for poly(dimethylsiloxane) having the lowest glass-forming temperature of any rubber, -110°C [1]. Secondary forces are harder to characterize because they operate between molecules or segments of the same molecule rather than being localized to a pair of atoms. These forces increase in the presence of polar groups and decrease with increasing distance between molecules. One can see qualitatively the effect of polarity on intermolecular attraction in the boiling points of the series methane (CH_4 , bp -161°C), methyl chloride (CH_3Cl , bp -24°C), and methyl alcohol (CH_3OH , bp 65°C). Because the energy of interaction varies inversely with the sixth power of the distance, small differences in structure can have large effects. For example, compare the boiling points of neopentane and *n*-pentane:

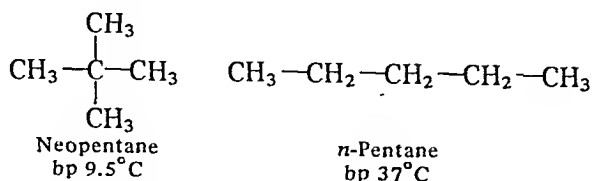
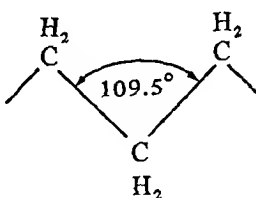
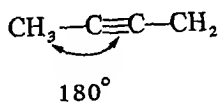
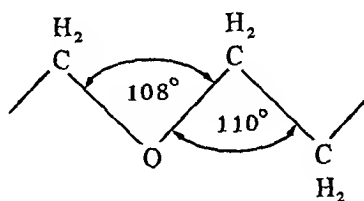
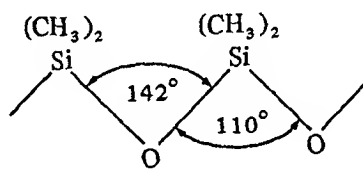
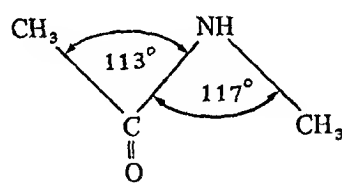
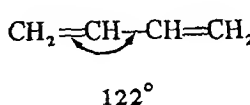
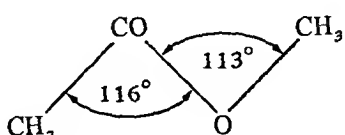


TABLE 2-1
Covalent Bonds

Dimensions and energies*					
Bond	Typical bond length, Å [2]	Typical average bond energy, kcal/mol [3]	Some typical bond angles [2]		
C—C	1.54	83			
C=C	1.34	147			
C≡C	1.20	194			
C—H	1.09	99			
C—O	1.43	84			
C=O	1.23	171			
C—N	1.47	70			
C=N	1.27	147			
C≡N	1.16	213			
C—Si	1.87	69			
Si—O	1.64	88			
C—S	1.81	62			
C=S	1.71	114			
C—Cl	1.77	79			
S—S	2.04	51			
N—H	1.01	93			
S—H	1.35	81			
O—H	0.96	111			
O—O	1.48	33			
Si—N	1.74	—			
					
					

*1 Å = 0.1 nm; 1 kcal = 4.185 kJ.

Intermolecular spacings can be estimated from crystal lattice dimensions in polymers and from the average density of amorphous polymers. Distances of 0.2 to 1.0 nm and energies of 2 to 10 kcal/mol predominate in small molecules. In a large molecule the energy is better characterized by the cohesive energy density, which measures the energy per unit volume rather than per molecule (see Sec. 2-5). The hydrogen bond deserves special mention because its effect is localized. Tables 2-1 and 2-2 summarize some typical values of bond energies and dimensions. Hydrogen bonding has a great

TABLE 2-2
Hydrogen Bonds [4]

Bond	Typical bond length, Å	Typical bond energy, kcal/mol
O—H—O	2.7	3 to 6
O—H—N	2.8	
N—H—O	2.9	4
N—H—N	3.1	3 to 5
O—H—Cl	3.1	
N—H—F	2.8	
N—H—Cl	3.2	
F—H—F	2.4	7

influence on the properties of cellulose (cotton) and polyamides (nylon and proteins), among others. The multiplicity of strong hydrogen bonds in dry cotton gives cotton many of the properties associated with a covalent-bonded *network* leading to insolubility and infusibility despite the fact that the truly covalent bonds give only a linear structure.

In general, covalent bonds govern the thermal and photochemical stability of polymers. Bond strength can be used as a clue to degradation mechanisms. For example, sulfur-vulcanized rubber is more likely to degrade at the comparatively weak —S—S— bonds than at the strong —C—C— bonds, both of which occur in the structure.

On the other hand, secondary forces determine most of the physical properties we associate with specific compounds. Melting, dissolving, vaporizing, adsorption, diffusion, deformation, and flow involve the making and breaking of intermolecular "bonds" so that molecules can move past one another or away from each other. In polymers the forces play the same role in the movements of individual segments of long-chain molecules.

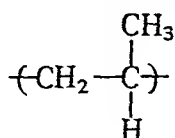
The *arrangement* of the covalent structure in space leads to a convenient method of classification that helps explain polymer properties. Basically there are two such arrangements. The polymer may be present as *single* molecules albeit of large individual size (i.e., mol wt of 10^7) or as an *infinite network*. The distinction is important because only the separate molecules can exhibit plastic flow and solubility. Accustomed as we are to thinking of the molecular scale as submicroscopic, it comes as something of a jolt to realize that the major portion of polymer in a tire or a bowling ball is really only one molecule. This is because all the separate molecules in the tire were connected to one another by sulfur cross-links during "vulcanization." (Incidentally, the molecular weight of a bowling ball polymer on this basis is about 10^{28} !)

One can calculate that a single molecule with molecular weight 10^6 and a density of 1 g/cm^3 should form a sphere 14.7 nm in diameter. This is large enough to be clearly visible by electron microscopy, and indeed such single molecules have been distinguished [5].

2-3 SINGLE MOLECULES

The single molecules may be *linear* or *branched* (Fig. 2-1). An important consequence is that branching interferes with the ordering of molecules, so that crystallinity decreases. Also, melt flow of branched molecules is more complicated by elastic effects.

If the polymer chain contains carbon atoms with two different substituents, the carbon is *asymmetric*, since the two parts of the chain with which it is connected are different also. Because carbon is tetrahedral, asymmetric atoms can exist in two different spatial configurations which are not interchangeable without breaking covalent bonds. Such *optical isomerism* is familiar in the organic chemistry of sugars, amino acids, and many other biologically important molecules. As an example, consider the case of polypropylene with the repeating unit:



Every other carbon is asymmetric. Three structures can result. These are best visualized by looking at the main polymer chain in an extended planar zigzag conformation. In general, changes in structure caused by rotations about single bonds are termed *conformations* and isomers that cannot be interchanged without bond breaking are termed *configurations*.

With polypropylene in the planar zigzag conformation, each pendant methyl group may be on one side of the chain, that is, all *d* or all *l*, using the terminology of stereochemistry. Using the terminology coined by Natta [6], this is an *isotactic structure* (Fig. 2-2). The regularity of such an arrangement facilitates the molecular order-

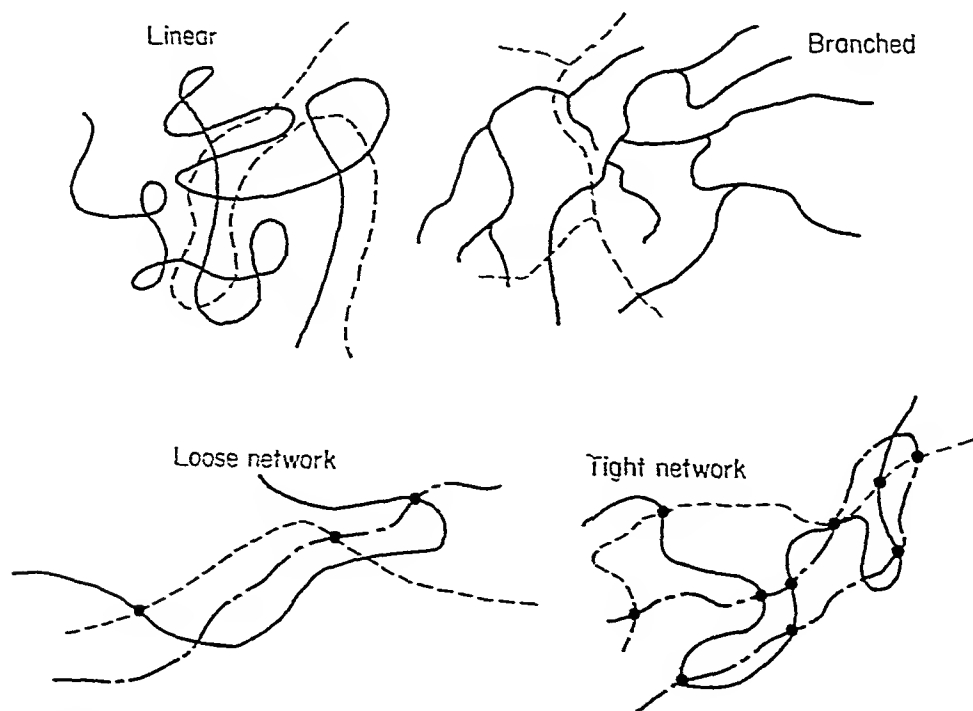
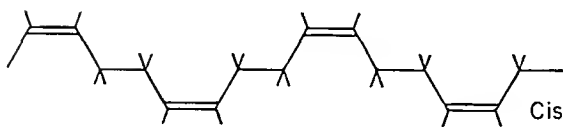
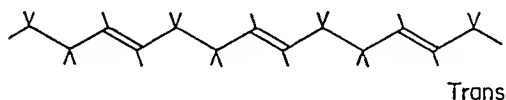
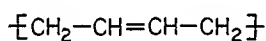
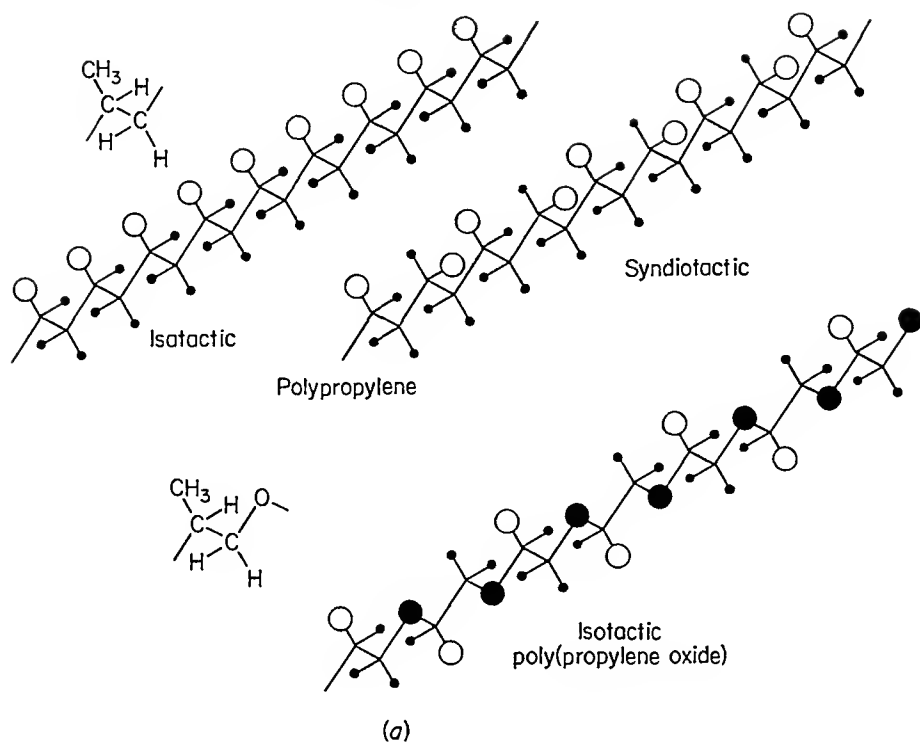


FIGURE 2-1
Polymer arrangements.

Stereoisomerism



(b)

FIGURE 2-2

(a) Stereoisomers from asymmetric carbon. (b) Stereoisomers from double bonds in chains of 1,4-polybutadiene.

ing necessary in crystalline materials. A regular alternation of pendant groups is called a *syndiotactic structure*. Random placement of the methyl group gives an *atactic structure*. Until the advent of coordination complex polymerization, it was difficult to produce synthetically (with an optically inactive catalyst) any structure except the atactic. However, these structures and more complex variants have since been produced with a variety of catalyst systems. In the amorphous, random-coil state, *tacticity* may be a minor factor in determining properties, but in crystal lattice formation it often assumes a predominant role.

Poly(propylene oxide) is an example of a polymer that has a three-atom repeat unit in the chain. It has been made as all *d* or all *l* isotactic polymers, which are optically active, as the *d-l* isotactic mixture, and as the atactic polymer. In the planar zigzag presentation the isotactic form has the pendant methyl group aligned in two rows (Fig. 2-2a).

A second type of stereoisomerism is of the cis-trans variety familiar in small ethenic molecules. Because rotation is not free about a double bond, the substituents on either side can assume two attitudes (Fig. 2-2b). When the chain parts are on opposite sides, we have a trans conformation, and when on the same side, cis. In this case also, the catalyst systems that permit production of all cis or all trans polymers have been developed only recently [6].

2-4 NETWORK MOLECULES

A loose polymer network can result from cross-linking a linear or branched polymer. Natural rubber consists mostly of a linear polymer that can be cross-linked to a loose network by reaction with 1 to 3% sulfur. The same polymer reacted with 40 to 50% sulfur is "hard rubber," a "tight" network polymer used for pocket combs and bowling balls (Fig. 2-1). Networks also may be formed directly, without the intermediate linear stage.

It was pointed out earlier (Sec. 2-1) that *thermoplastic* polymers soften without chemical change when heated and harden when cooled, whereas *thermosetting* polymers once formed do not soften upon heating below their decomposition temperatures. We can identify the thermoplastic polymers with the linear and branched structures. The thermosets generally form network polymers upon being heated the first time. As with all generalizations in the field of polymers, there are numerous exceptions. Cellulose is essentially a linear polymer (cotton, rayon). However, because of the strong hydrogen-bonded structure, softening does not occur below the decomposition temperature. Therefore it cannot be molded without breaking bonds.

A more complex arrangement results when two polymers form networks that overlap in space. One way of making such an *interpenetrating network* (IPN) is to swell a cross-linked polymer with a monomer. The IPN comes about when the monomer is polymerized into a second network, even though the two networks may have no covalent bonds in common [7, 8, 9]. Despite the fact that two polymers are not compatible when mixed as linear molecules, the IPN may exhibit no macroscopic phase separation and thus can be much stronger than a mechanical mixture.

Another kind of mixed network comes about when two linear polymers that are incompatible at room temperature are simultaneously cross-linked at a high temperature at which they are compatible. Phase separation on cooling may be inhibited by the covalent bonds, which limit movement of polymer chains. The term *semi-IPN* can refer to a linear polymer trapped in a network of another polymer. In the older literature these were sometimes called by the colorful term *snake-cage* systems.

2-5 COHESIVE ENERGY DENSITY

It has been mentioned before that many of the unique properties of polymers can be attributed to the fact that polymer segments are held together by covalent bonds in

one direction but by secondary bonds in the other two. A measure of the strength of secondary bonds is given by the cohesive energy density (CED):

$$\text{CED} = \frac{\Delta E_v}{V_l} \quad (2-1)$$

where ΔE_v is the molar energy of vaporization and V_l is the molar volume of the liquid. For small molecules, ΔE_v can be measured by conventional means. The energy necessary to separate molecules from one another from the close spacing typical of the liquid state to the distant spacing of the vapor is evaluated directly by calorimetric methods or indirectly by measuring the vapor pressure p as a function of absolute temperature T . The Clapeyron equation can be used to extract an enthalpy of vaporization ΔH_v :

$$\frac{dp}{dT} = \frac{\Delta H_v}{T(V_g - V_l)} \quad (2-2)$$

where V_g and V_l are the molar volume of the compound in the vapor and liquid at temperature T . The internal energy of vaporization ΔE_v is related by

$$\Delta E_v = \Delta H_v - p(V_g - V_l) \quad (2-3)$$

Another useful parameter is the square root of the CED, the *solubility parameter* δ . In quoting values of these terms, the dimensions must be given. The most widely accepted unit for solubility parameter is the Hildebrand, which is equal to $1 (\text{cal/cm}^3)^{1/2}$. Of course, a Hildebrand is also $2.046 (\text{J/cm}^3)^{1/2}$. Solubility parameters for some common liquids are listed in Table 2-3. Liquids with like solubility parameters are apt to dissolve the same solutes and to be mutually compatible. This leads to an indirect method of measuring δ for a polymer. The dissolving of a polymer in a low-molecular-weight liquid causes the random coil to expand and occupy a greater volume than it would in the dry, amorphous state. If the polymer is composed of single molecules, viscous flow can occur, and the viscosity will be increased as the polymer expands. It is expected that when the polymer and solvent have the same δ , the maximum expansion will occur and therefore the highest viscosity (for a given concentration) will be obtained. By measuring the viscosity of solutions of the same polymer at the same concentration (usually dilute) in a variety of solvents, one should be able to deduce a consistent value of δ_2 for the polymer. If the polymer comprises a cross-linked network, solution cannot occur, but individual parts of the polymer chains, i.e., polymer segments, can solvate to give a swollen gel. Once again, it is expected that the maximum swelling will take place when δ_2 matches δ of the solvent.

Although the foregoing statements are borne out qualitatively by experiment, specific interactions and differences in molar volume of solvent make the estimation of δ_2 more complicated. An example is the swelling of a cross-linked butyl rubber [11] in 10 solvents (Fig. 2-3). In this figure, v_2 is the volume fraction of rubber in the swollen sample. It is obvious that solvents with δ between 8.0 and 9.5 swell butyl rubber more effectively than do solvents with δ below 8.0 or above 9.5.

TABLE 2-3
Characteristic Parameters for Some Solvents at 25°C [10]

Solvent	Solubility parameter, Hildebrands, (cal/cm ³) ^{0.5}	Hydrogen bonding index	Molecular weight	Density, g/cm ³
Acetone	10.0	5.7	58.08	0.792
Acetonitrile	11.9	4.5	41.05	0.786
Acrylonitrile	10.5	4.3	53.06	0.806
<i>n</i> -Amyl alcohol	8.5	8.9	88.15	0.817
Aniline	11.8	8.7	93.13	1.022
Benzene	9.2	2.2	78.11	0.879
<i>n</i> -Butanol	11.4	8.9	74.12	0.806
<i>tert</i> -Butyl alcohol	10.5	8.9	74.12	0.789
Carbon disulfide	10.0	2.2	76.14	1.266
Carbon tetrachloride	8.6	2.2	153.82	1.594
Chlorobenzene	9.5	2.7	112.56	1.106
Chloroform	9.3	2.2	119.38	1.492
Cyclohexane	8.2	2.2	84.16	0.774
Cyclohexanone	9.9	6.4	98.15	0.951
<i>n</i> -Decane	6.6	2.2	142.27	0.726
Diethyl carbonate	8.8	4.0	118.13	0.969
Diethylene glycol (DEG)	14.2	8.5	106.12	1.116
DEG, monobutyl ether	8.9	6.9	162.23	0.955
DEG, monoethyl ether	9.6	6.9	134.18	0.988
Diethyl ether	7.4	6.9	74.12	0.714
<i>N,N'</i> -Diethylpiperazine	15.4	9.4	142.16	—
Diisopropyl ether	6.9	6.6	102.18	0.725
<i>N,N</i> -Dimethylacetamide	10.8	6.6	87.12	0.937
<i>N,N</i> -Dimethylformamide	12.1	6.4	73.10	0.944
Dimethyl sulfoxide	13.0	5.0	78.13	1.096
1,4-Dioxane	9.9	5.7	88.11	1.028
Ethyl acetate	9.1	5.2	88.11	0.901
Ethanol	12.8	8.9	46.07	0.785
Ethylbenzene	8.8	2.7	106.17	0.863
Ethylene carbonate	14.7	4.0	88.06	1.321
Ethylene dichloride (or 1,2-dichloroethane)	9.8	2.7	98.96	1.246
Ethylene glycol (EG)	14.6	9.6	62.07	1.113
EG, monobutyl ether or (2-butoxyethanol)	8.9	6.9	118.18	0.901
EG, monoethyl ether or (2-ethoxyethanol)	9.9	6.9	90.12	0.925
Ethylene oxide	11.1	5.8	44.05	0.887
2-Ethylhexanol	9.5	8.9	130.23	0.829
Formamide	19.2	16.2	45.04	1.133
Furfural	11.2	4.7	96.09	1.160
Glycerol	16.5	8.5	92.10	1.261
<i>n</i> -Heptane	7.4	2.2	100.21	0.680
<i>n</i> -Hexane	7.3	2.2	86.18	0.655
Isophorone	9.4	7.0	138.21	0.923
Isopropyl acetate	8.4	5.3	102.14	0.872
Isopropyl alcohol	11.5	8.9	60.10	0.800
Kerosene (typical)	7.2	2.2	—	0.800
Methylene chloride	9.7	2.7	84.93	1.315
Methyl ethyl ketone	9.3	5.0	72.11	0.800

TABLE 2-3
Characteristic Parameters for Some Solvents at 25°C [10] (Continued)

Solvent	Solubility parameter, Hildebrands, (cal/cm ³) ^{0.5}	Hydrogen bonding index	Molecular weight	Density, g/cm ³
Nitrobenzene	10.0	3.2	123.11	1.200
Nitroethane	11.1	3.1	75.07	1.045
Nitromethane	12.7	3.1	61.04	1.131
1-Nitropropane	10.3	3.1	89.10	0.996
2-Nitropropane	9.9	3.1	89.10	0.983
<i>n</i> -Pentane	7.0	2.2	72.15	0.626
Perchloroethylene or tetrachloroethylene	9.3	2.2	165.83	1.631
Piperidine	8.7	10.9	85.15	0.861
Propionitrile	10.8	5.0	55.08	0.777
<i>n</i> -Propyl alcohol	11.9	8.9	60.10	0.800
Propylene glycol or (1,2-propanediol)	15.0	9.4	76.10	1.036
Propylene oxide	9.2	5.8	58.08	0.829
Pyridine	10.7	8.7	79.10	0.978
Styrene	9.3	2.7	104.14	0.901
Tetrahydrofuran	9.1	5.3	72.11	0.889
Toluene	8.9	3.8	92.14	0.862
1,1,2-Trichloroethane	9.6	2.7	133.41	1.440
1,1,2-Trichloroethylene	9.3	2.5	131.39	1.462
1,1,1-Trichloro-2,2,2-trifluoroethane	7.2	2.5	187.38	1.563
VM and P Naphtha	7.6	2.2	—	0.750
Water	23.5	16.2	18.02	0.997
Xylene (mixed)	8.8	3.8	106.17	0.868

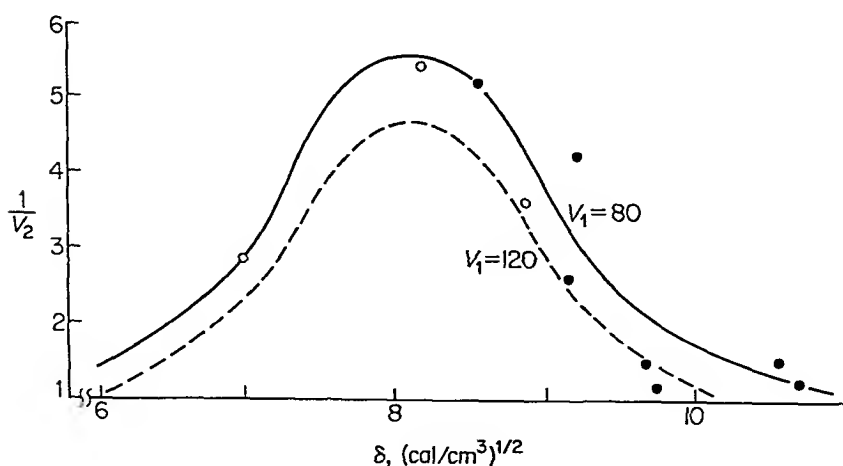


FIGURE 2-3

Swelling data for butyl rubber [11] in solvents with $100 < V_1 < 120$ (○) and with $80 < V_1 < 100$ (●). Curves for Eqs. (2-5) and (2-6) with $\beta_1 = 0.45$, $N = 1.0 \times 10^{-4}$, and $\delta_2 = 8.1$.

The free-energy change on mixing solvent and polymer, ΔF_m , can be written as

$$\Delta F_m = RT[N_1 \ln(1 - v_2) + N_2 \ln v_2 + \chi N_1 v_2] \quad (2-4)$$

where N_1 and N_2 are the moles of solvent and polymer, respectively, v_2 is the volume fraction of polymer in the mixture, R is the gas constant (Boltzmann's constant per mole), and T is the absolute temperature. The *polymer-solvent interaction parameter* χ characterizes the interaction energy per mole of solvent divided by RT for a specific solvent-polymer pair. In a swollen gel there is a change in free energy also due to the elastic deformation of the polymer network.

At equilibrium the partial molar free energy of the solvent in the gel equals that of pure solvent. Using this fact and noting that the elastic energy term depends on N , the number of polymer chains per unit volume, and on V_1 , the molar volume of the solvent, Flory [12] derives an equation that equates the mixing term (on the left) with the elastic term (on the right):

$$\ln(1 - v_2) + v_2 + \chi v_2^2 = -NV_1 \left(v_2^{1/3} - \frac{v_2}{2} \right) \quad (2-5)$$

While this equation is not a fundamental definition of χ , it has been used to derive experimental values of χ from swelling data. Orwoll [13] has reviewed the theoretical basis for χ and the experimental procedures for its measurement. Osmotic pressure, vapor sorption, gas-liquid chromatography, and several other methods can be used. Although it may not be the best absolute measure of χ , equilibrium swelling is a very practical method and relates directly to an important application, namely, the selection of materials for use in the presence of solvents.

The calculation of v_2 from known values of the other variables is simplified by recourse to a nomograph (Fig. 2-4). It is customary to calibrate the value of χ for a given solvent-polymer pair by using a sample that has had its cross-link density measured by an absolute method such as stress-strain behavior together with the rubber elasticity equation (Sec. 8.2). Some values of χ are listed in Table 2-4 for polymers in "good" solvents.

To connect Eq. (2-4) with δ , several semiempirical approaches have been tried. One approach is [11]:

$$\chi = \beta_1 + \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \quad (2-6)$$

where δ_1 and δ_2 relate to the solvent and polymer, respectively, R is the gas constant, and β_1 is a lattice constant, usually 0.35 ± 0.1 . Combination of Eqs. (2-5) and (2-6) gives the curves drawn in Fig. 2-3. Representative values of δ_2 (Table 2-5) obtained from swelling data show an increase with the polarity of the polymer. Another use of solubility parameters is in choosing compatible polymers for use in blends in surface coatings and adhesives. Maximum compatibility is expected to occur between polymers with the same δ_2 . Because the variation of V_1 is not enough to reduce the scatter in plots of this type, other molecular parameters have been sought to categorize

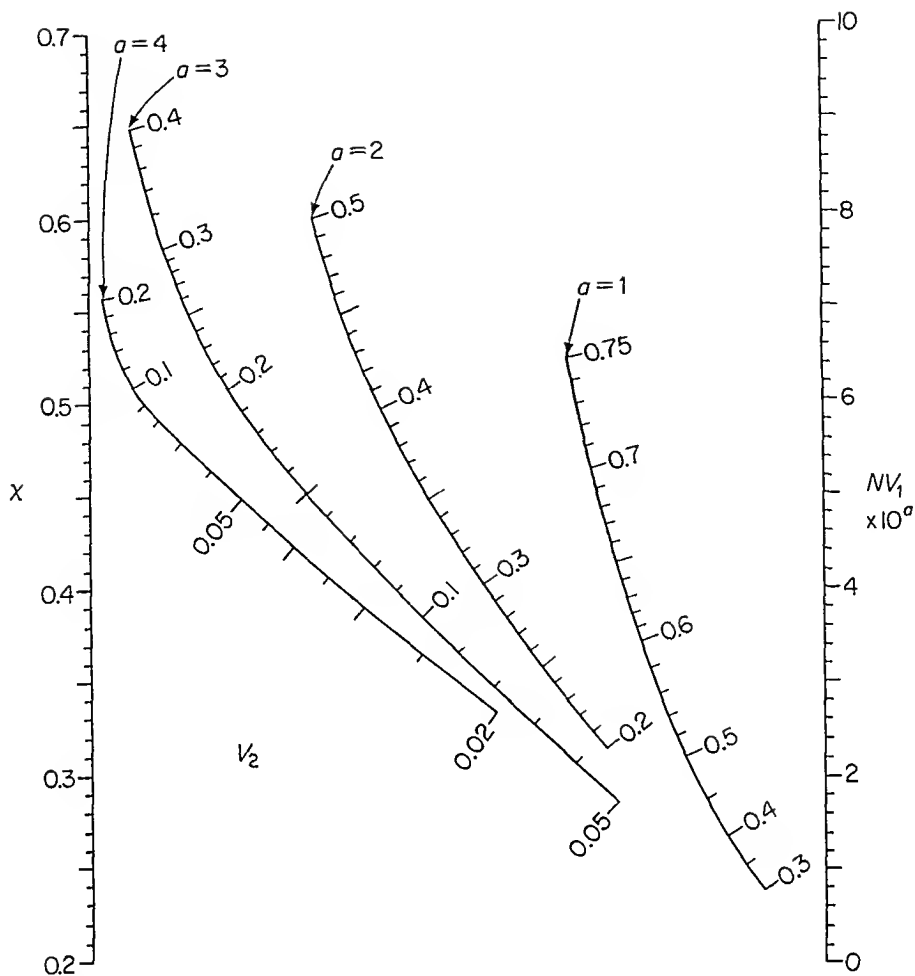


FIGURE 2-4

Nomograph for swelling Eq. (2-5). A straight line connects the compatible values of the three variables on their corresponding scales. Note that the exponent a varies with the scale selected for v_2 . For example, when $\chi = 0.40$ and $v_2 = 0.3$, $NV_1 = 4.0 \times 10^{-2}$.

TABLE 2-4
Polymer-Solvent Interaction Parameters at 25°C [11]

Polymer	Solvent	Interaction parameter χ
<i>cis</i> -Polyisoprene	Toluene ($V_1 = 106$)*	0.391
	Benzene ($V_1 = 89.0$)	0.437
Polyisobutylene	Toluene	0.557
	Cyclohexane ($V_1 = 108$)	0.436
Butadiene-styrene (71.5 : 28.5)	Benzene	0.442
	Cyclohexane	0.489
Butadiene-acrylonitrile 82 : 18	Benzene	0.390
70 : 30	Benzene	0.486
61 : 39	Benzene	0.564

* V_1 is in cubic centimeters per mole. See references 13, 14, and 15 for more examples.

TABLE 2-5
Solubility Parameters of Polymers [16, 17]

Polymer	δ_2	Polymer	δ_2
Alkyd, med.-oil length	9.4	Poly(vinyl chloride)	9.7
Cellulose derivatives:		Poly(vinylidene chloride)	12.2
C. dinitrate	10.6	Polystyrene	9.1
C. lacquer nitrate	11.5	Poly(tetrafluoroethylene)	6.2
C. diacetate	10.0	Rubbers:	
Ethyl cellulose	10.3	Butadiene-acrylonitrile (70:30)	9.4
Ester gum	9.0	Butadiene-styrene (71.5:28.5)	8.1
Nylon 66	13.6	<i>cis</i> -Polyisoprene	8.3
Polyacrylonitrile	15.4	Polychloroprene	9.2
Polyethylene	7.9	Polybutadiene	8.6
Polypropylene	8.1	Polyisobutylene	8.1
Poly(ethylene terephthaaate)	10.7	Ethylene-propylene	8.0
Poly(methyl methacrylate)	9.5	Poly(dimethylsiloxane)	7.3
Poly(vinyl acetate)	9.4	Polysulfides	9.0 to 9.4

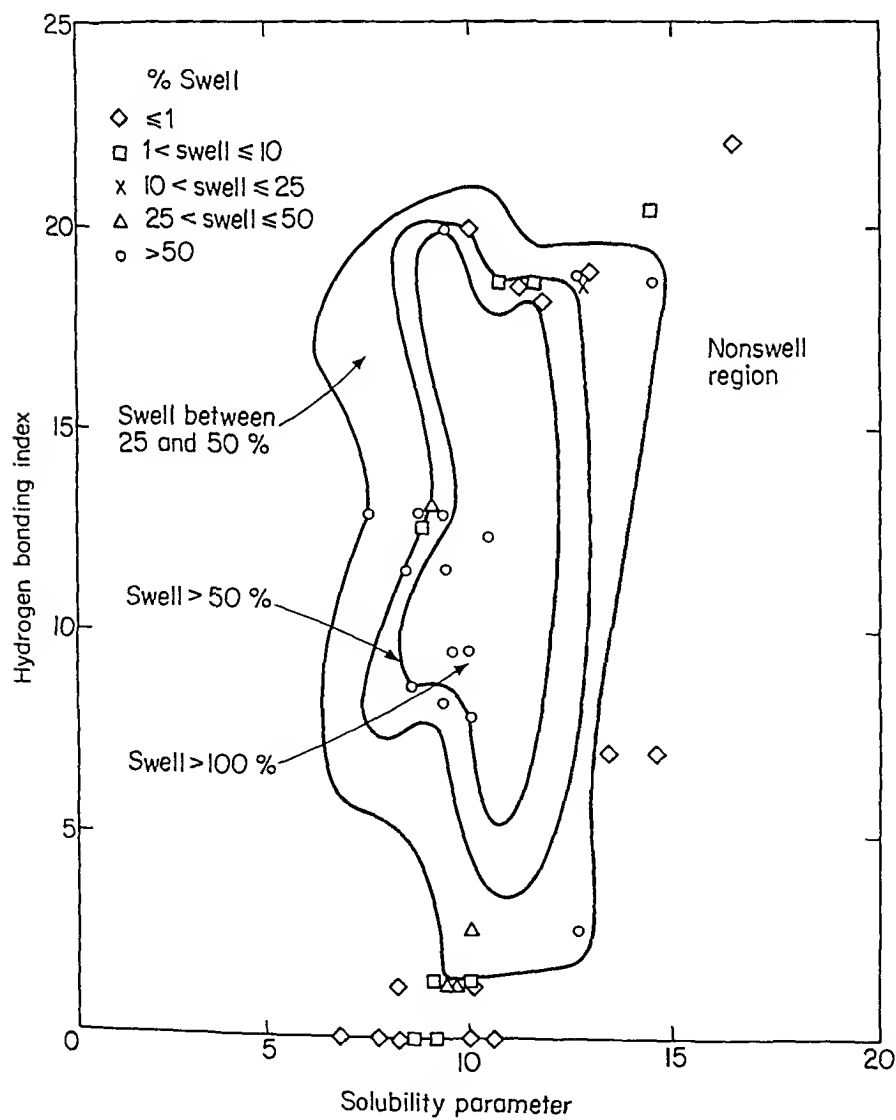


FIGURE 2-5
Swelling of cross-linked fluorocarbon rubber [17].

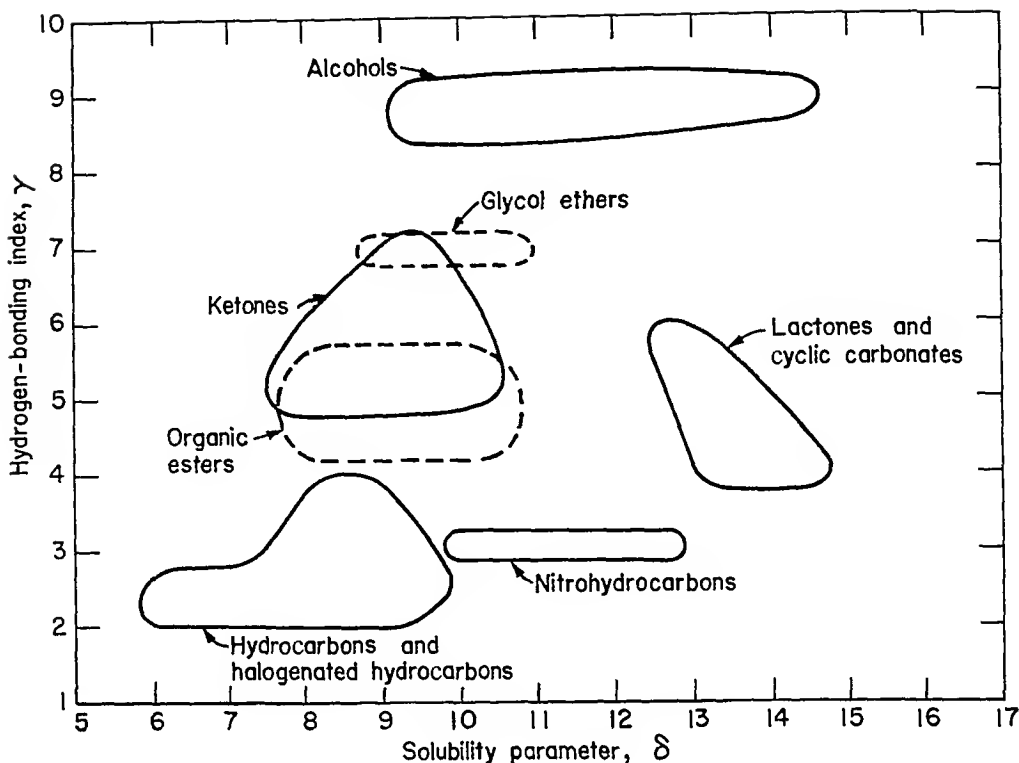


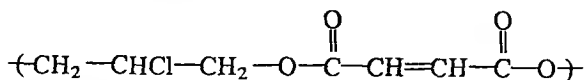
FIGURE 2-6

Parameter locations for major solvent groups [10].

solvent behavior further. The change in hydrogen bonding that occurs when a solvent is mixed with deuterated methanol in specific proportions compared with the bonding when benzene is the solvent can be measured by the shift of a peak in infrared spectrum away from a value of 2681 cm^{-1} . By using a scale for hydrogen-bonding parameter that ranges from 0 for benzene and other hydrocarbons to 18.7 for ethanol and up to 39.0 for water, swelling and compatibility of polymers and solvents can be better predicted than by using δ alone. A two-dimensional plot for the swelling of a sample of cross-linked fluorocarbon rubber (Fig. 2-5) has contour lines at constant swell ($\text{swell} = 1/v_2$). Values of the relative hydrogen-bonding index for various solvents appear in Table 2-3. The parameter locations for some major groups of solvents are indicated in Fig. 2-6. Such a map has great value in selecting solvents for a coating system or in judging probable resistance to swelling for a particular application.

PROBLEMS

- 2-1. For a material with a density of 1.0 g/cm^3 , estimate the molecular weight of a sphere made up of one molecule with a diameter of (a) $100 \text{ \AA}$, (b) 1.0 micron , and (c) 1.0 cm . Avogadro's number = 6.02×10^{23} molecules/mol.
- 2-2. A polyester has the following repeat unit:



What stereoisomers are possible?

- 2-3. Estimate the repeat distance between methyl groups in the same row of isotactic poly(propylene oxide) in the planar zigzag form (Fig. 2-2a). Repeat for the syndiotactic poly(propylene oxide).
- 2-4. A cross-linked sample of polyisobutylene swells 10 times its original volume in cyclohexane. What volume will it swell to in toluene?
- 2-5. A polymer of propylene oxide, $\text{-(CH}_2\text{CH(CH}_3\text{)O)-}$, is cross-linked so that the average distance between cross-links is 5000 chain atoms. The polymer density after cross-linking is 1.20 g/cm^3 . What is the density of a swollen sample in a solvent for which $\chi = 0.40$ and solvent density is 0.80 g/cm^3 ? Assume additivity of volumes. Molecular weight of solvent is 102.
- 2-6. The gamma radiation of many polymers results in cross-linking. For a new polymer, assuming that cross-link density $N/2$ is directly proportional to radiation dose, deduce the cross-link density at the highest dose and χ , the interaction parameter.

Dose, Mrad	v_2 in <i>n</i> -hexane at 25°C
1	0.090
2	0.110
4	0.138
8	0.177
16	0.225

- 2-7. Calculate the extended length (in nm) of a molecule with 1000 repeat units of



Neglect the end-group contributions to length.

- 2-8. A single molecule of isotactic polypropylene has a molecular weight of 2×10^6 . Calculate
- (a) The length in cm when the chain is extended (planar zigzag form).
 (b) The volume occupied if the molecule forms a single crystal with a density of 0.906 g/cm^3 .
- 2-9. A cross-linked rubber sample swells to 10 times its original volume when immersed in solvent A. Assuming that this is the best possible solvent for the polymer, what is the solubility parameter of solvent B, which is made up by adding a small amount of a lactone to solvent A? The sample swells only to 5 times its original volume B. Both solvents A and B have a molar volume of 100 cm^3 and the same lattice parameter β_1 . All tests are made at 27°C . Solvent A: $\text{CED} = 85.0 \text{ cal/cm}^3$, $\chi = 0.33$.
- 2-10. A mixture of benzoyl peroxide (0.5 g) with poly(vinyl ethyl ether) (100 g) is heated to 175°C . Assuming that all the peroxide decomposes and that each molecule of peroxide extracts two hydrogen atoms to produce a single cross-link, calculate:
- (a) The expected chain density N at 25°C in the final network.
 (b) The swollen volume of 1 cm^3 of polymer in benzene at 25°C .
- Benzoyl peroxide, mol wt = 242. PVVE, mol wt = 72 (repeat unit), $\rho = 0.97 \text{ g/cm}^3$. V_1 (benzene) = $89.0 \text{ cm}^3/\text{mol}$. χ (PVVE, benzene) = 0.40.
- 2-11. A silicone rubber sample is cross-linked by exposure to gamma radiation. The average number of chain atoms between cross-links is determined by a mechani-

cal test to be 850. What volume (cm^3) will be occupied by 1 g of rubber when it is equilibrated in *n*-octane at 20°C ? The formula weight for dimethyl siloxane $\text{-(Si(CM}_3)_2\text{O)-}$ is 78. The solid rubber has a density of 1.00 g/cm^3 . The formula weight of *n*-octane is 114 and its density is 0.703 g/cm^3 . χ (20°C) is 0.49.

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3

PHYSICAL STATES AND TRANSITIONS

3-1 PHYSICAL STATES

The physical states in which a polymer can exist can be idealized by considering first a long, regular polymer chain consisting of a succession of single bonds. Polyethylene, poly(styrene), or poly(methylene oxide) might serve as an example. With free rotation around each bond, the chain can assume an infinite number of conformations in space. During these rotations the bond angles and distances remain fixed. Three extreme conditions are possible.

1. *Completely free rotation.* This keeps the molecules in continuous motion. The wriggling molecules can slip past one another rather easily. This is a polymer *melt*. The higher the temperature, the more intense the molecular motion.
2. *No rotation.* At some sufficiently low temperature, rotation around single bonds becomes impossible because of the energy barriers that a substituent on one chain atom encounters when trying to move past the substituent on an adjacent chain atom. Even hydrogen atoms on adjacent carbons interfere with one another at low enough temperatures. The polymer molecules become trapped in a chaotic, disordered, entangled state. This is a *glass*.
3. *Packing.* Polymer molecules may fit together in such a way that intermolecular attractions stabilize the chains in a regular lattice even though there are negligible intramolecular barriers to rotation around single bonds. This is the *crystalline* state of "long-range" order. If the temperature is lowered so that intermolecular barriers to rotation become great, the crystal is even more stable.

Each of these is an idealization. Factors that modify the picture are:

1. The polymer chain may contain double or triple bonds or rings, which do not permit rotation at any temperature without actual bond breaking.
2. The polymer may be branched or cross-linked.

3. The polymer may be short or long.
4. The polymer may not be homogeneous; parts may be in various states.
5. The polymer may be dissolved in a lower molecular weight liquid or in another polymer.
6. A polymer that is stressed may be oriented and not completely isotropic in the melt. Rapid cooling of the melt may preserve the orientation even when the stress is removed.

Two major transition temperatures are the glass transition temperature, T_g , and the melting temperature, T_m . T_g is the temperature below which free rotations cease because of intramolecular energy barriers. Values of T_g most often listed for polymers correspond to the stiffening temperature. Simple bending of a rod might be the criterion. The time scale of the test is important. Even hindered rotation around single bonds may be sufficient to allow adjustment to new conformations over a long time. A plastic that is brittle when hit with a hammer may sag under its own weight over a period of weeks at the same temperature. It is a glass in the first test, but a melt (of sorts) in the second.

Although we have described the glass as being homogeneous, many researchers challenge the idea. The interpretation of some results with microscopy and diffusion experiments suggests instead that glasses are made up of tiny, ordered *domains* with dimensions on the order of 5 to 15 nm.⁴ However, application of other techniques such as neutron scattering and light scattering have not confirmed the existence of the domains. The subject remains a very controversial one [1, 2].

If the long polymer chains are interconnected by widely separated cross-links, the segments between the cross-links can still assume the three states mentioned. In the case of state I, a loosely cross-linked melt is called a *rubber*. The extent to which the original molecules can assume new conformations is limited by the finite extensibility of segments between cross-links. If the number of cross-links is increased, the segments become shorter. Finally, the segments may be so short that rotations around single bonds are no longer possible and the system resembles a permanent glass even at temperatures where an uncross-linked polymer would be a melt.

The difficulty of fitting an entire polymer into a lattice leads to a generalization that crystallinity is never perfect. In fact, many "crystalline" polymers may have amorphous contents of 20 to 50%. This is many orders of magnitude greater than the imperfections associated with common metals. The amorphous portion may be glass, melt, or rubber, depending on temperature, time-scale of testing, or cross-linking.

Another conceptual difficulty that may arise concerns the previously discussed phenomenon of tacticity (Sec. 2-3). Free rotation around single bonds does not imply interchangeability of two substituents on a chain atom. Thus an isotactic polymer (as in Fig. 2-2) may undergo an infinite number of rotations around each of the bonds in the main chain. However, when the chain is once again put in the planar zigzag form, all of the pendant groups will fall into exactly the same positions they had before the rotations.

Before going on to discuss in greater detail the characteristics of these three basic states (glass, melt, and crystal), it might be well to describe some interrelations. Since no long-range molecular rearrangement is possible below T_g , it follows that if crystals

are to form, crystallization will have to take place above that temperature. The highest temperature at which a crystal lattice is stable is the melting temperature, T_m . If no crystal lattice is stable, or if the material is quenched from the melt to a temperature well below T_g , behavior of the sort indicated by line $A-B$ (Fig. 3-1) is possible. Ordinary atactic polystyrene and poly(methyl methacrylate) are two polymers that do not form crystals and, on cooling below their T_g 's (both about 100°C), go directly from an easily deformed melt to a rigid, transparent, amorphous glass. Common nylon (nylon 66) quenched to room temperature might follow the same path. However, if the nylon is cooled at a constant rate (say $1^\circ/\text{s}$) from the melt, it might follow path $A-C$. Some crystals form when the temperature falls below T_m . At a temperature below T_g , the crystals that form are surrounded by a matrix of amorphous glass. If the glass is the major constituent, the material may be quite brittle. When polyethylene is cooled to room temperature, it remains well above its T_g . As indicated by line $A-D$, the polymer may be highly crystalline with amorphous melt outside the crystalline regions. In response to a stress, the amorphous parts are rather easily deformed. Of course, above T_m there are no crystals. Figure 3-2 is another attempt to interrelate the various physical states. Compositions C and D are near points c and d , respectively, in Fig. 3-2. It is possible to have a melt with low crystallinity (point c'). If the crystals are large enough and strong enough to act as massive cross-links connecting high-molecular

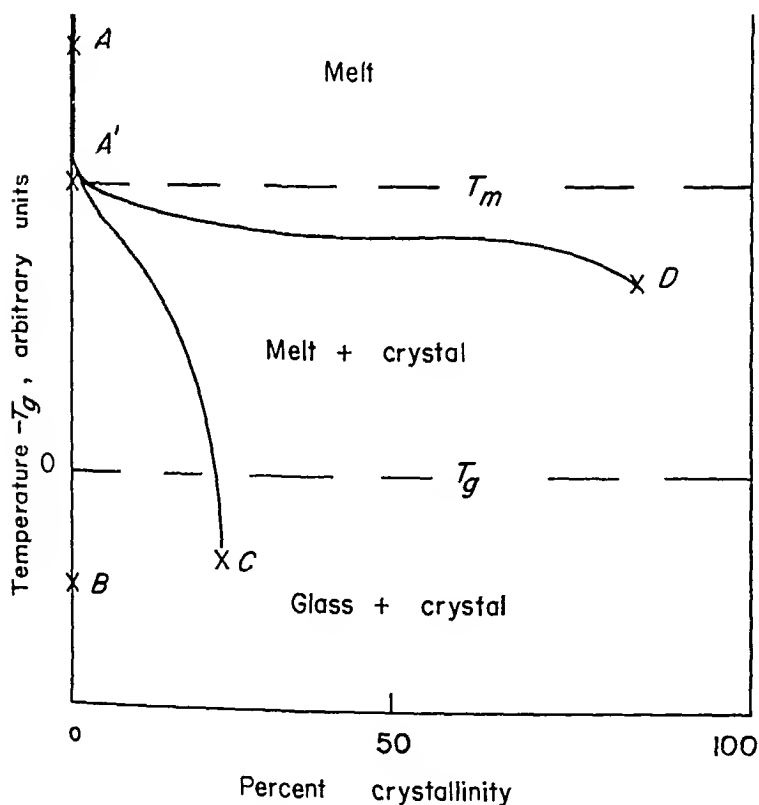


FIGURE 3-1

Examples of cooling from the melt (point A): All curves go through A' on cooling. B : Room temperature state of polystyrene cooled at any rate from the melt. Also, typical state of nylon 66 that has been quenched from melt to a temperature below T_g . C : Typical final state of nylon 66 cooled at $1^\circ\text{C}/\text{s}$ to a temperature below its T_g . D : Linear polyethylene cooled to room temperature (which is well above its T_g).

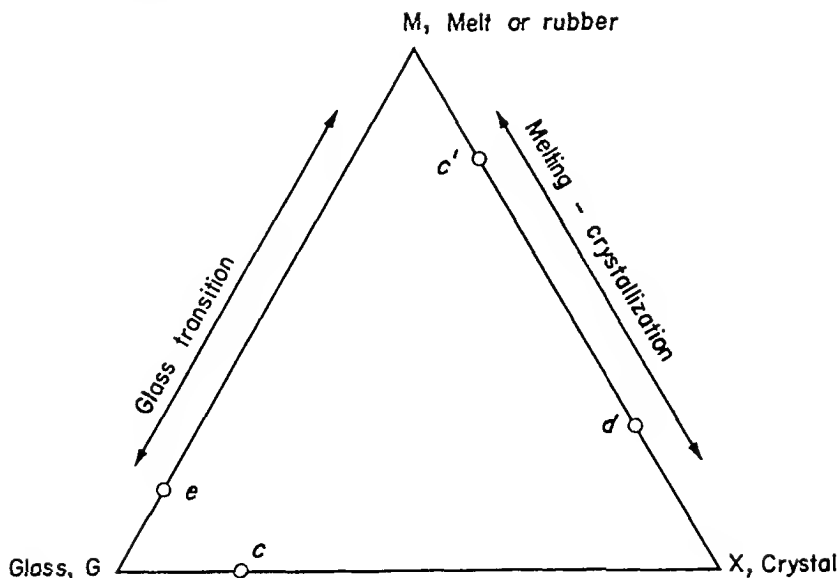


FIGURE 3-2

Composition diagram. Point c corresponds to C of Fig. 3-1, d to D , and c' to C' . Compositions c or c' may be rubbery even in the absence of covalent cross-links. Point e is possible only when two portions of the same molecule have separate values of T_g .

segments, the melt will act like a rubber as long as the temperature is between T_g and T_m . A composition in which parts of molecules can be glassy while other parts remain in the melt (point e) is achieved by the technique of block copolymerization (Sec. 4-7). Once again, rubbery behavior is attainable if the glassy domains act as cross-links. Such a polymer is really two homopolymers tied together each exhibiting its own T_g . Because they are tied together, they cannot segregate macroscopically, but can only do so on a microscopic basis. The thermoplastic elastomer based on styrene and butadiene is one commercial example of a system with two T_g 's, one below room temperature, the other above (see Sec. 13-3).

3-2 AMORPHOUS POLYMERS

An amorphous polymer is easy to imagine. A bowl of spaghetti is a fair analogy. A bucket of worms is even better, because polymer molecules are constantly in motion. To be analogous to some common polymers, the worms would have to be 10^3 to 10^4 times longer than they are thick (that is 5 mm diameter, 10 m long!). Obviously, the constant motion one notes in the bucket is not of whole worms at once, but of individual segments. The analogous *segmental Brownian motion* in polymers is very important in explaining flow and deformation. As previously mentioned, the segments themselves move by virtue of rotations around single bonds in the main chain of the polymer. The intensity of the motion increases with temperature. Below a certain temperature (T_g) the polymer segments do not have sufficient energy to move past one another. Rotations around single bonds become very difficult. If the material is stressed, the only reversible response can be for bond angles and distances to be strained, since no gross movements of segments can take place. Such a material is a

glass. Only if the temperature is above T_g can the segments rearrange to relieve an externally applied stress. This important parameter, T_g , can be characterized also as an inflection point in the specific volume-temperature curve (Fig. 3-3). The *glass-transition temperature* T_g resembles a second-order transition, because the change in volume is not discontinuous as it is with T_m . The abruptness of the transition can be rationalized by the concept of free volume (see Sec. 3-3). The segmental energy has to exceed a certain barrier value before a "hole" of segmental dimensions can be created for diffusion.

Whether or not T_g is a thermodynamic parameter is the subject of debate. A statistical thermodynamic model put forward by Gibbs and DiMarzio [4] predicts the existence and some of the characteristics of the glass transition. Still, attempts to verify the thermodynamic interrelation among changes in heat capacity, expansion coefficient, and compressibility at T_g have met with only occasional success [5]. Experimentally, T_g itself depends on the time scale of the experiment in which it is measured. As pointed out by Bueche [6], a 100-fold increase in heating rate when volume change is being measured increases the apparent T_g of polystyrene only about 5°C . Molecular weight affects T_g also. Theoretical equations of some complexity have been proposed [7]. An empirical correlation can be obtained in the form

$$T_g = T_{g,\infty} - \frac{K_g}{M_n} \quad (3-1)$$

where T_g for a finite molecular weight M_n is related to that for an infinitely long polymer, $T_{g,\infty}$. For example, the data of Beevers and White [7] for poly(methyl methacrylate) can be fitted by $K_g = 2.1 \times 10^5 \text{ }^\circ\text{C}\cdot\text{mol/g}$ and $T_{g,\infty} = 114^\circ\text{C}$ when

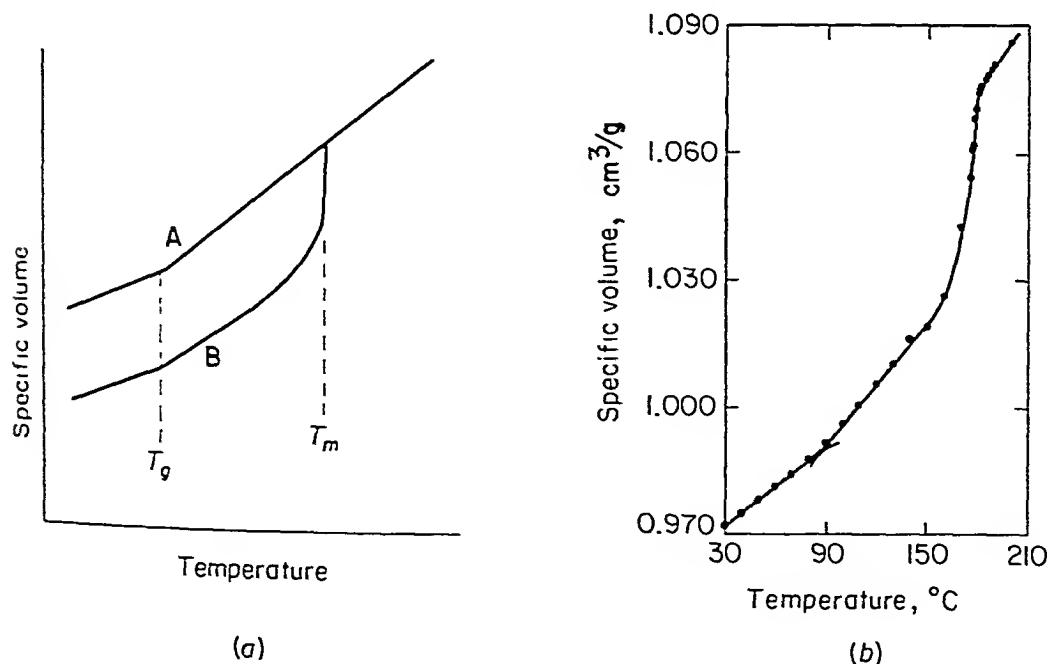


FIGURE 3-3

(a) Specific volume vs. temperature for A, an amorphous polymer, and B, a partly crystalline polymer. (b) Volume-temperature curve for pure poly(N,N' -sebacoyl piperazine), for which T_g is 82°C and T_m is 180 to 181°C [3].

M_n exceeds 10^4 . Likewise, polystyrene data are fitted by $K_g = 1.7 \times 10^5 \text{ }^\circ\text{C}\cdot\text{mol/g}$ and $T_{g,\infty} = 100^\circ\text{C}$ down to molecular weights of less than 3×10^3 [6]. In both cases the maximum difference in T_g due to differences in M_n are small above $M_n = 5 \times 10^4$.

If we store energy in an amorphous polymer by stressing it and then attempt to recover the work we put in, there is always a certain amount of hysteresis or mechanical loss. This loss may be small above or below T_g , but it is always a maximum at T_g . In fact, this often is a more sensitive measurement than volume change on heating. The rationalization is not difficult. In the glass the stress is stored by bond distortions, which are easily recovered. Above T_g , polymer chains can be uncoiled from their random conformation by rotations readily about successive single bonds. Only at T_g is the uncoiling hindered by intermolecular forces. The discussion of deformation and flow of amorphous polymers is continued in Chaps. 7 and 8.

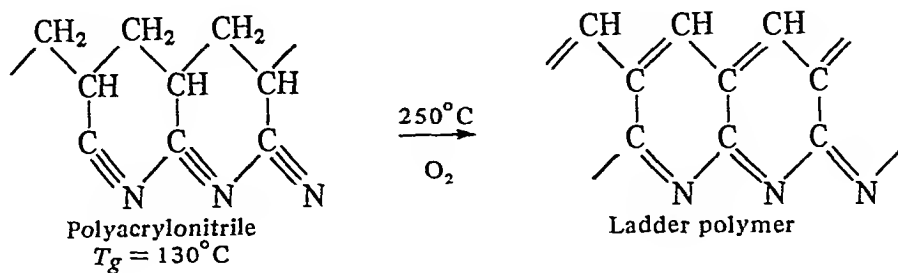
Segmental mobility is highly dependent on chain stiffness and somewhat dependent on intermolecular forces. It is expected that polymers with high polarity or high cohesive energy density should have higher transition temperatures than non-polar materials. This is borne out approximately in Table 3-1. On the other hand, regularity, which is so important to crystallizability, counts for little in the amorphous transition. Since the segmental motion implies the concerted movement of many chain atoms (10 to 50 atoms), bulky side groups, which hinder rotation about single bonds, should raise T_g also. An interesting series in this respect is afforded by the vinyl ether polymers. As the polar ether linkage is diluted by longer alkyl side groups from methyl to butyl, T_g decreases. However, when the alkyl group is bunched up next to the chain, as with *tert*-butyl ether, rotation about the single bonds in the chain is made difficult and T_g is raised dramatically. Chain stiffness and, consequently, T_g are increased if single bonds in the polymer chain are replaced by multiple bonds about

TABLE 3-1
Typical Transition Temperatures [9]

Polymer	$T_m, ^\circ\text{C}$	$T_g, ^\circ\text{C}$	Solubility parameter δ_2^*
Poly(dimethyl siloxane)	-54	-123	7.3
Polyethylene	137	-120(?)	7.9
Polyisobutylene	—	-70, -60	8.1
<i>cis</i> -Polyisoprene	28	-70	8.3
Polychloroprene	80	-50	9.2
Poly(vinyl acetate)	—	29	9.4
Poly(vinyl chloride)	212	87	9.7
Poly(methyl methacrylate)	—	105	9.5
Polystyrene	240 (isotactic)	100, 105	9.1
Poly(vinyl methyl ether)	144	-20, -10	
Poly(vinyl ethyl ether)	86	-25	
Poly(vinyl <i>n</i> -butyl ether)	64	-52	
Poly(vinyl isobutyl ether)	115	-5, -18	
Poly(vinyl <i>tert</i> -butyl ether)	260	-8	
Poly(ethylene terephthalate)	267	69	10.7
Cellulose tributyrate	183	120	
Ethyl cellulose	—	43	10.3

* Solubility parameter in $(\text{cal}/\text{cm}^3)^{1/2}$ taken from Table 2-5.

which there can be no rotation. Ring structures in the main chain contribute inflexibility as in poly(ethylene terephthalate) or cellulose derivatives. "Ladder" polymers have been synthesized in which there are no single bonds in the polymer chain. For example, pyrolysis of polyacrylonitrile gives an aromatic structure of high thermal stability:



This particular material is so stable that it can be held directly in a flame in the form of woven cloth and not be changed physically or chemically [8]. For a copolymer in which the monomer units are distributed in a random fashion, polarity and chain stiffness of the copolymer are roughly the average of those for the individual homopolymers. It is not surprising, then, that very often the glass-transition temperature of a copolymer can be predicted from a knowledge of the weight fraction w of each monomer and the T_g of each homopolymer. Two empirical equations are popular [9]:

$$T_g(\text{copolymer}) = w_1(T_g)_1 + w_2(T_g)_2 \quad (3-2)$$

$$\frac{1}{T_g(\text{copolymer})} = \frac{w_1}{(T_g)_1} + \frac{w_2}{(T_g)_2} \quad (3-3)$$

3-3 PLASTICIZATION

The glass-transition temperature marks the onset of segmental mobility for a polymer. We can picture the movement of the segments due to a concentration gradient (diffusion) or due to a stress (viscous flow) as a jumping phenomenon. A segment moves or diffuses in a concerted manner into a vacancy or hole adjacent to it, leaving a hole of like dimensions behind. We know that the specific volume of a polymer increases as the temperature increases, as shown by the normal coefficient of expansion. However, the increase in volume is not uniform, and the local density on a molecular scale fluctuates to give an overall population of holes or "free volume." As previously mentioned, one experimental method of determining T_g is to note the temperature at which the coefficient of expansion changes. This greater increase in volume with temperature above T_g represents the addition of free volume for segmental movement. In Sec. 7-5, a quantitative measure of "free volume" is given in the form of the Williams, Landel, and Ferry (WLF) equation.

If we mix two materials of different T_g 's, we can imagine that each would contribute to the free volume of the system in proportion to the amount of material present. In this way we can rationalize that T_g should be a linear function of composition for copolymers. Likewise if we mix a polymer with a solvent or another compatible polymer, we expect a T_g that is the weighted average of each component

[Eq. (3-2) or (3-3)]. An important application of this principle is in plasticization. A plasticizer is a nonvolatile solvent that usually remains in the system in its ultimate use. Since solvent and polymer are not chemically bound to one another, the term "external plasticizer" is sometimes used to distinguish this case from copolymerization, where a comonomer of low T_g may be used to lower the T_g of the system (so-called internal plasticization). Poly(vinyl chloride) is very versatile because it is compatible with a variety of plasticizers and because the plasticized polymer remains quite stable both physically and chemically for long periods of time. The linearity of T_g with composition for several plasticizers is indicated by the behavior of the *flex temperature*, which is close to T_g for amorphous polymer (Fig. 3-4). The efficiency in lowering T_g is not the only criterion for selecting a plasticizer. Cost, odor, biodegradability, high temperature stability, and resistance to migration may be important in specific applications. Since stiffness of a polymer at temperature T decreases as $T - T_g$ increases, plasticization efficiency may be judged also by the lowering of the stiffness modulus at room temperature (Fig. 3-5).

Many commercial fibers are plasticized by small amounts of water. The familiar process of ironing a garment generally takes place between T_g and T_m so that creases can be controlled without destroying the overall structure due to crystallinity. In steam ironing, moisture lowers T_g , allowing a lower ironing temperature.

3-4 CRYSTALLINITY

Polymers in the solid state can be completely amorphous, partially crystalline, or almost completely crystalline. Polymer crystals have the requirement that they must

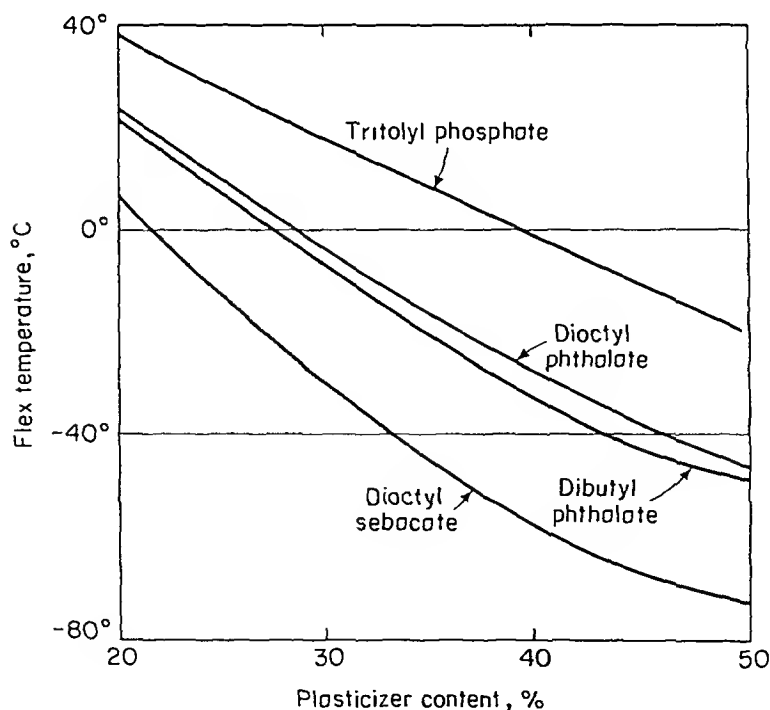


FIGURE 3-4

Effect of plasticizers on cold flex temperature of poly(vinyl chloride) compounds. The temperature is that at which torsional stiffness reaches some arbitrary value [10].

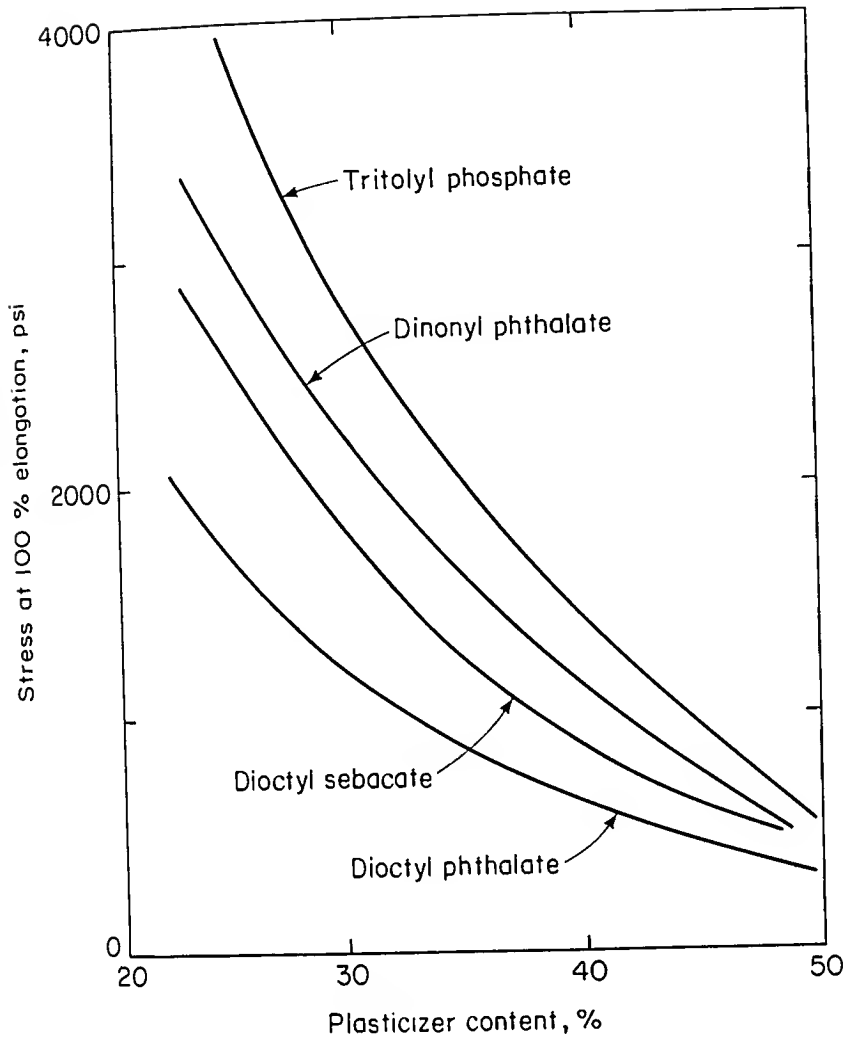


FIGURE 3-5

Effect of plasticizers on 100% modulus (stress at 100% elongation) of poly(vinyl chloride) compounds [10].

accommodate the covalent axis within an ordered structure. For some time the interpretation of x-ray diffraction patterns was that individual polymer molecules were partly crystalline and partly amorphous. The longest dimension of the crystallites in polycrystalline materials is usually about 5 to 50 nm, which is a small fraction of the length of a fully extended polymer molecule. A graphical representation of this once popular model is shown in Fig. 3-6. Here a long polymer chain wanders successively through disordered, random regions, through bundles of organized regions (micelles), again amorphous, again ordered, and so on. For a polymer that can be extended to a length of 5,000 nm with crystal and amorphous domains averaging 10 nm, a single polymer thread might tie together a hundred or more crystallites. This "fringed micelle" model is inadequate in some ways. The abrupt change in density from crystal to amorphous region at the end of the micelle is unlikely. If some of the chains can fold on themselves, the transition to amorphous region can be accommodated. Such chain-folding is clearly seen in single crystals.

For many years the statement could be made that all polymer crystals were submicroscopic. However, Till [11] and Keller [12] in 1957 produced single crystals of polyethylene up to 10 μm in one dimension. Subsequently, single crystals of

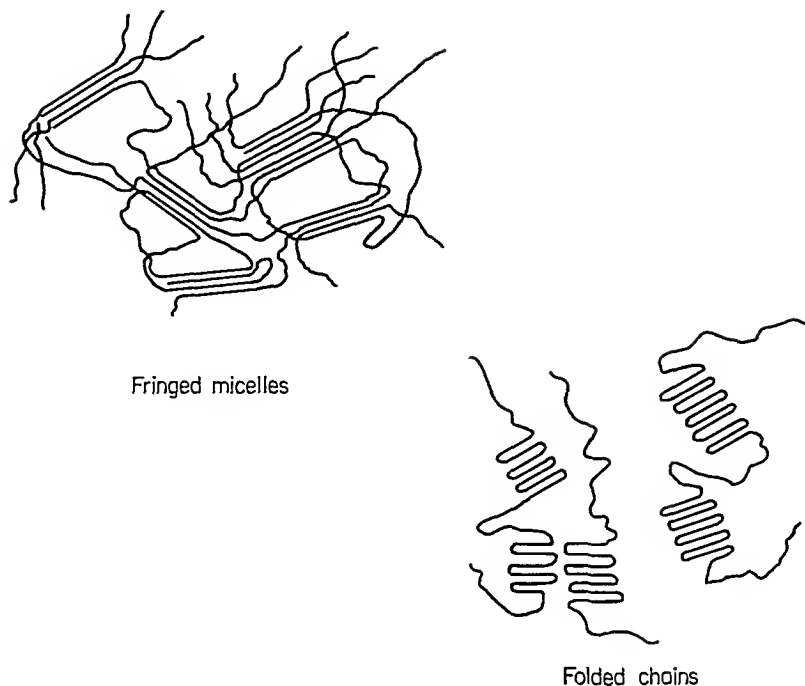


FIGURE 3-6
Crystallite arrangements.

several other materials were obtained. Morrow mentions nylon 6, polypropylene, polybutene, and poly(4-methyl pentene-1) [13]. A surprising feature of most of these crystals is that the covalent axis of the polymer chains is perpendicular to the longer dimensions of the crystals (Fig. 3-7). The explanation is that the polymer folds over on itself after about a hundred chain atoms have entered the lattice. The crystal thickness increases with the temperature of crystal formation or with subsequent annealing at a higher temperature. A polyethylene crystal with a thickness of 10 nm may be formed at 100°C. Heating the crystal at 130°C for several hours will increase the thickness to about 40 nm.

Both thermodynamic and kinetic arguments have been propounded to explain the spontaneous formation of the folded-chain structure [14]. The kinetic theory currently favored by some workers views the folding as a means of increasing the crystallization rate, even though crystals with completely extended chains might be more stable under equilibrium conditions. Indeed, polyethylene samples with molecular weights of less than 10,000 exhibit crystal thicknesses approximating the length of extended chains [15]. The four-sided hollow-pyramidal crystal is only one form found for polyethylene. Ridged crystals, truncated pyramids, and fibrillar forms are known also. Other materials show other features. Poly(oxymethylene) gives flat hexagonal crystals and polypropylene gives lathlike crystals. Polypropylene is an example where the folded chains are not derived from planar zigzag ribbons but from helices (see next section). The single-crystal evidence showing folded-chain structures for a variety of polymers leads one to think that the same structures occur in polycrystalline materials also.

The mechanical properties of crystalline materials can be viewed from two extreme positions. Materials of low crystallinity may be pictured as essentially amorphous polymer with the crystallites acting as massive cross-links, about 5 to 50 nm in diameter. The cross-links restrain the movement of the amorphous network just as covalent cross-links would. On the other hand, unlike the covalent bonds, the crystal cross-links can be melted or mechanically stressed beyond a rather low yield point. At the opposite end of the crystallinity spectrum, one can regard a highly crystalline material as a pure crystal that contains numerous defects such as chain ends, branches, folds, and foreign impurities. Mechanical failure of highly crystalline nylon, for example, bears a great resemblance to that of some metals, with deformation bands rather than the ragged failure typical of amorphous polymers.

X-ray and electron-diffraction studies of unoriented polymers allow the calculation of some interplanar distances in the crystalline domains. Diffraction by oriented fibers gives more information, since the axis of the fiber usually parallels one of the crystallographic axes. Both the conformation of single chains and the arrangement of the chains in the crystal lattice can be deduced, although the methods of analysis are neither simple nor unambiguous.

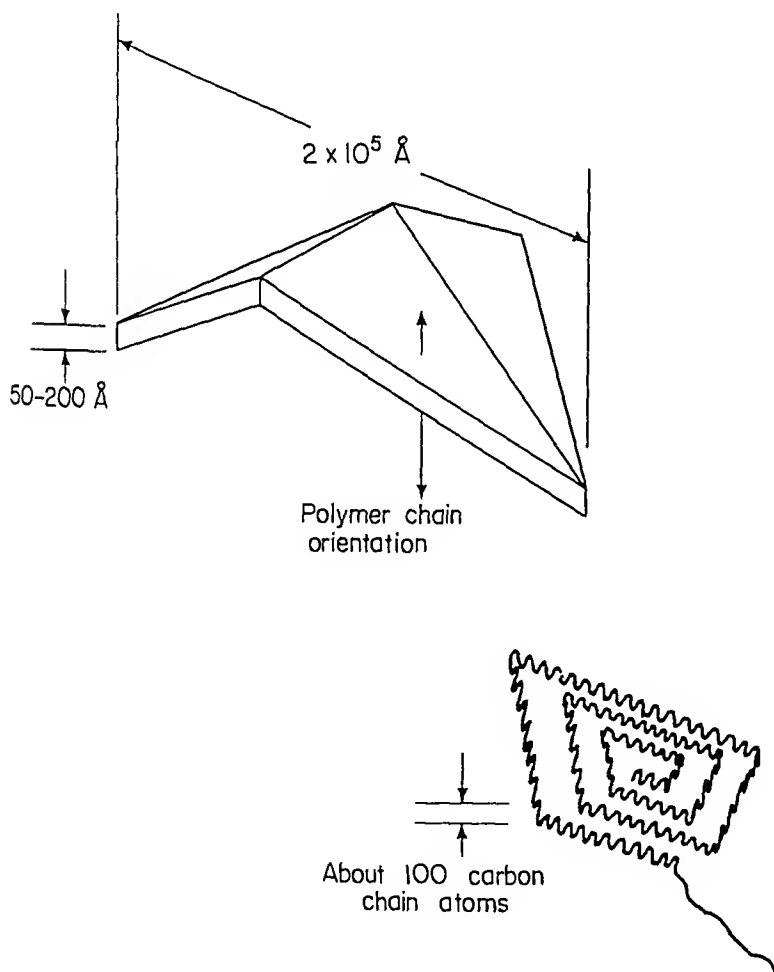


FIGURE 3-7

A large single crystal of polyethylene might have the dimensions indicated here. The growth mechanism involves the folding over of the planar zigzag chain on itself at intervals of about every 100 chain atoms. A single crystal may contain many individual molecules.

3-5 CONFORMATION OF SINGLE CHAINS IN CRYSTALS

The planar zigzag conformation has been used to illustrate tacticity (Sec. 2-3). Some polymers assume this conformation in the crystal, e.g., polyethylene and 1,4-*cis*-polybutadiene. Isotactic polymers in which the pendant group is bulky often assume a helical form [16]. Polypropylene forms an $H,3_1$ helix, i.e., a helix in which three monomer units give one complete turn (Fig. 3-8). This simple helix can be generated by imagining the successive bonds being wrapped around a triangular mandrel, every other bond lying on a face and the alternating bonds lying on an edge. As seen in an end view (Fig. 3-8), the pendant methyl groups form a second triangular prism that contains the smaller one. Helices with more than three repeat units per turn are common. The α -helix assumed by many polymers of amino acids has about eighteen units per five turns. This helical form for the single molecule may persist even in solution.

Other helices are favored by syndiotactic polymers and by some symmetrically substituted materials. A helix designated as $H,2_1$ can be generated by wrapping a chain around a mandrel with a square cross section (Fig. 3-9). Unlike the previous helices, the $H,2_1$ has bonds only on faces and not on the edges of the mandrel. It must be emphasized that only single-bond rotations and not bond bending or stretching are involved in achieving these conformations. Specific interactions between pendant groups, such as hydrogen bonding in polymers of amino acids, or specific hindrances, such as repulsion between adjacent pendant methyl groups, often dictate the conformation with the most favorable free energy.

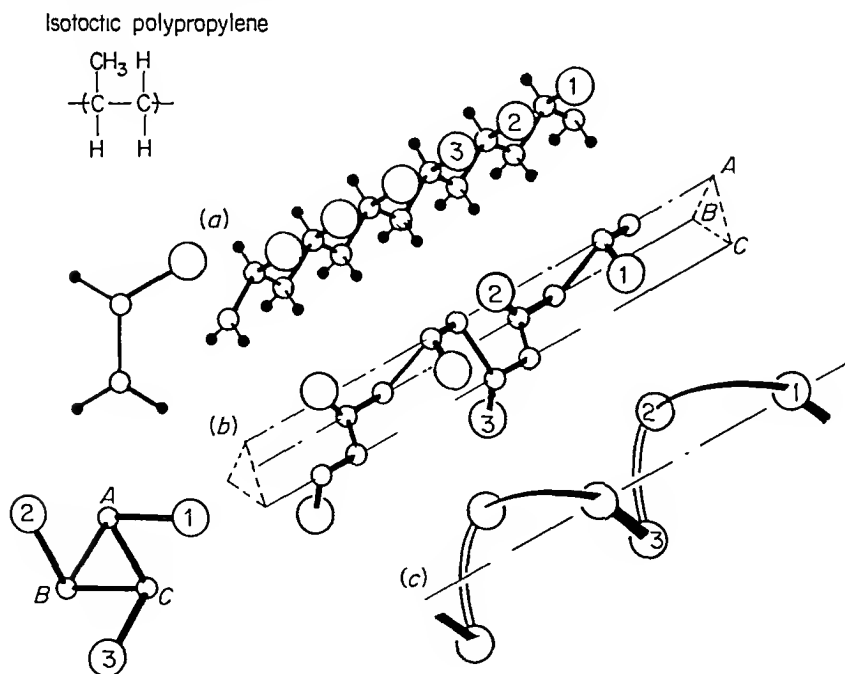


FIGURE 3-8

(a) Isotactic polypropylene. The large spheres represent the pendant methyl groups. (b) The $H,3_1$ helix with hydrogens omitted. (c) The pendant methyl groups as a helix [17].

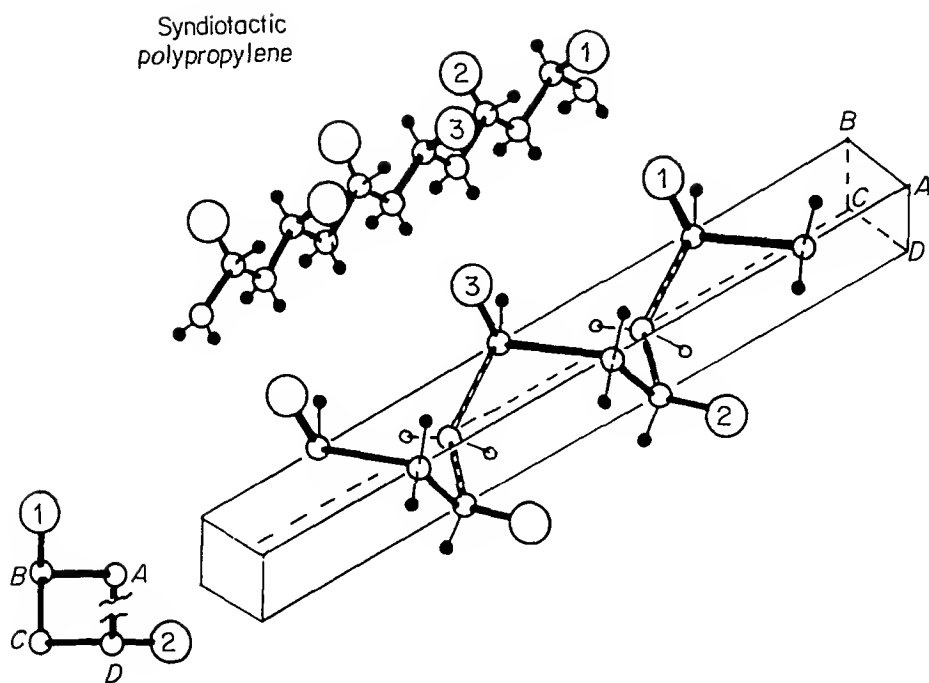


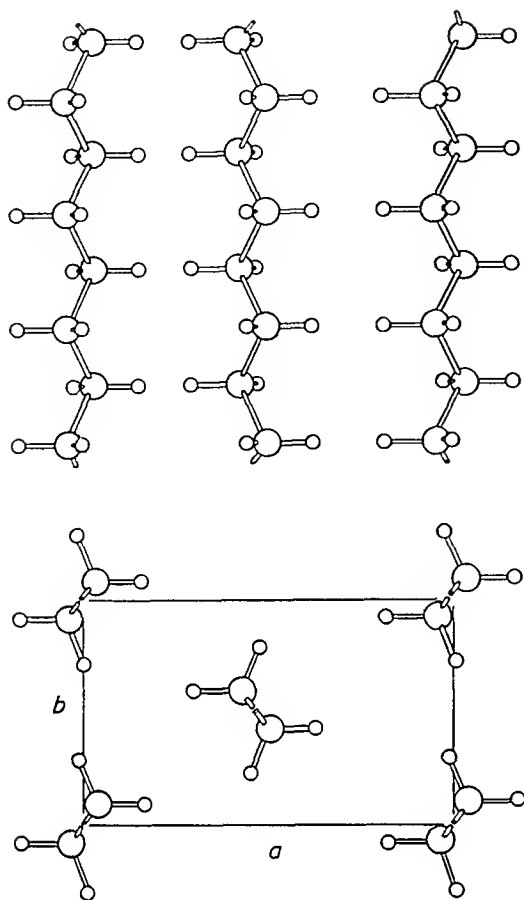
FIGURE 3-9
The $H_{2,1}$ helix of syndiotactic polypropylene [17].

The fitting together of the chains in a lattice can take many forms. The unit cell of polyethylene (planar zigzag chains) is shown in Fig. 3-10. With some polymers, especially atactic, polar ones, crystallites may be formed that are lamellar. For example, they may have a helical form as individual chains and pack into a lattice in one direction, but not have a well-defined periodicity in the third dimension.

3-6 SPHERULITES AND DRAWING

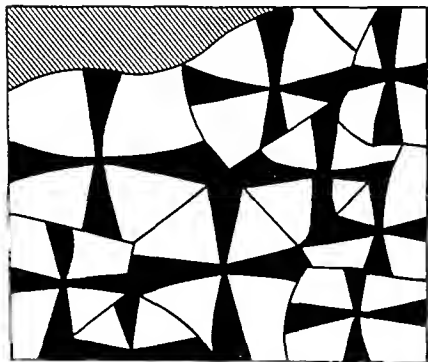
Quiescent crystallization of a polymer from the melt or solution often results in a peculiar form of crystallite growth with a preferred chain orientation relative to a center (nucleus). For example, cooling poly(ethylene oxide) in a thin film results in the growth of circular areas emanating from nuclei, the growth stopping only when advancing fronts meet. When completely cooled, the areas may be as large as a centimeter in diameter (Fig. 3-11). Polarized light reveals that the polymer chains are oriented tangentially around each nucleus despite the fact that the area (a "spherulite," since it extends in three dimensions) consists of a multitude of crystallites and is not a single crystal. In most materials the spherulites do not exceed $100\ \mu\text{m}$ in diameter.

When a highly crystalline material is stressed, a certain amount of energy can be stored by bond bending and stretching and other lattice distortions. Beyond the elastic limit (usually at a low elongation), rearrangement of the polymer chains often takes place so that chains are oriented in the direction of stress. This destroys the spherulitic pattern if it exists. This process of orientation by stretching (*drawing*) is used for most textile fibers (nylon, rayon, polyacrylonitrile). The oriented crystalline structure gives high strength and low elongation in the direction of the fiber axis. Drawing of crystal-

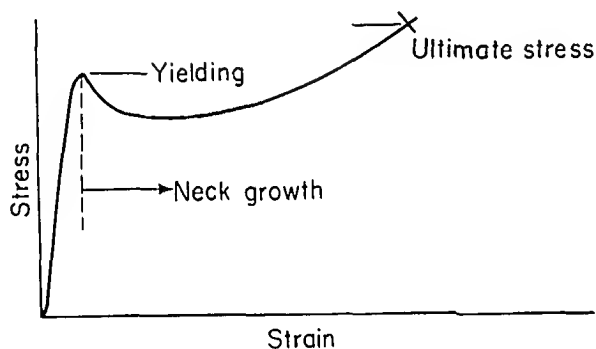
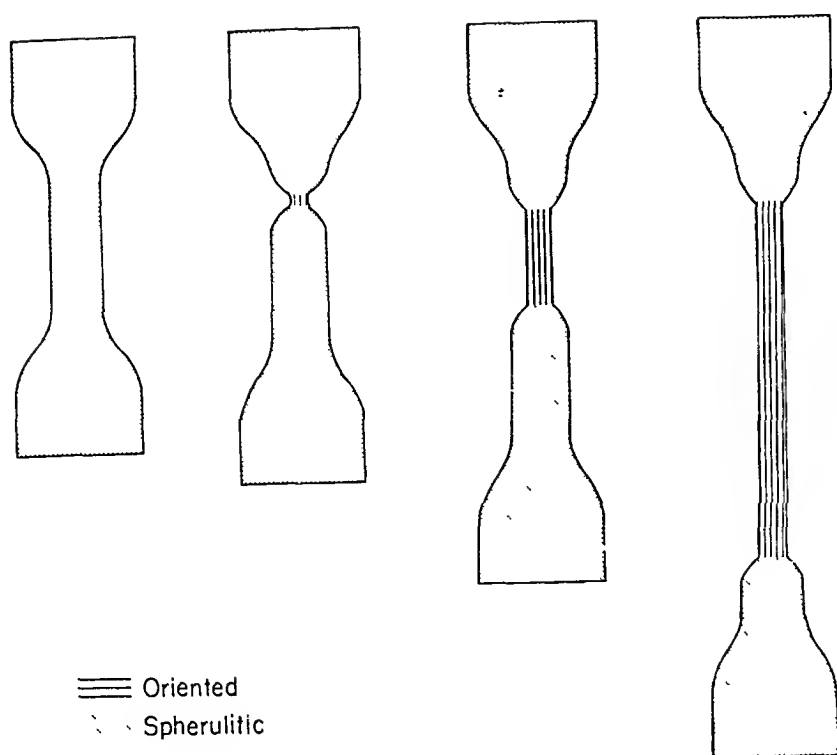
**FIGURE 3-10**

Model of the packing in the crystal structure of polyethylene in which $a = 7.41 \text{ \AA}$, $b = 4.94 \text{ \AA}$, and successive pendant atoms are $2.55 \text{ \AA}$ apart along the chain axis [18].

line materials often has another unusual feature, *necking*. If a sample of spherulitic nylon is stretched, elongation does not occur uniformly over the whole sample as it does when a rubber band is stretched. After a slight overall elongation (*ca.* 5%), a neck appears (Fig. 3-12) and grows if stretching is continued. Spherulites at the shoulder are pulled apart, and polymer chains are oriented in the direction of stress

**FIGURE 3-11**

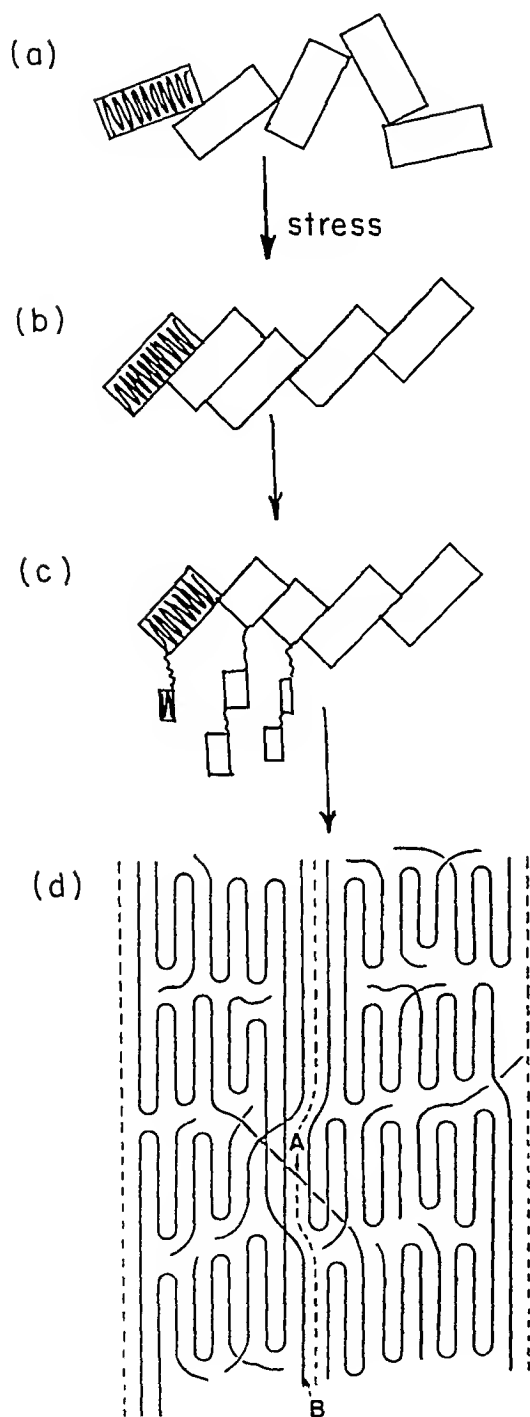
Spherulitic structure of a crystalline polymer seen between crossed polarizing sheets.

**FIGURE 3-12**

Successive stages in the drawing (elongation) of a spherulitic polymer.

as they enter the neck. The orientation is permanent, since the new crystalline form is stable. Thus, it is not inconsistent that molded (spherulitic) nylon may be listed as having an elongation at break of about 300%, while drawn nylon fiber (oriented) has an ultimate elongation of only 20%. However, in drawn polyethylene, folded chains persist in oriented crystallites with tie molecules connecting the folded chain packets (Fig. 3-13).

The process just described involves going from random crystallites (short-range order, long-range disorder) to oriented crystallites (short- and long-range order). There are numerous polymers, which although amorphous in the unstressed state, on uniaxial stretching exhibit sharp x-ray patterns characteristic of oriented crystals. Usually the pattern disappears on release of the stress as the polymer goes back to the amorphous state. Characteristic repeat distances from x-ray patterns of these and stable crystalline materials allow estimation of unit cell dimensions, the crystal system, and also the ultimate density of perfectly crystalline material.

**FIGURE 3-13**

The drawing process. (a) Twisted crystal lamellae that make up the spherulitic structure are pulled into (b) tilted pre-deformed lamellae during the pre-necking period. (c) The tilted lamellae are torn into blocks and tie molecules that make up the microfibrils (d) with interfibrillar A and intrafibrillar B tie molecules in the fully drawn state as proposed for polyethylene by Peterlin [19].

The organization of the crystals in a spherulite has been investigated for numerous materials. For example, single crystals have been observed to grow faster in one direction than another with branching so as to assume a sheaflike appearance and ultimately to form the nucleus of a spherulite [14]. The individual arms of the spherulite may have twists that lead to concentric rings or bands. More commonly the nucleus of a spherulite is a solid impurity such as a catalyst residue. Such adventitious nuclei can be augmented or obscured by intentionally adding materials to act as nuclei. This can result in highly crystalline materials with spherulites so small as not to scatter light appreciably. "Nucleated" materials are available commercially, where the mechanical advantages of crystallinity are desired without the opacity that comes from light scattering at the boundaries of large spherulites.

When crystallization occurs under stress, interesting new forms are seen. In particular, nucleation along flow lines in polyethylene results in a "shish kebab" structure, so-called because folded chain lamellae (the "kebabs") grow out at intervals from a center shaft of oriented polymer. While not all are as dramatic as the polyethylene case, "row structures" in which a central fibril acts as a contiguous source of nuclei are not uncommon when crystallization takes place in extrusion and molding, even under conditions of low melt stress [20].

3-7 CRYSTALLIZATION

The tendency for a polymer to crystallize is enhanced by *regularity* and *polarity*. The molecules must fit together neatly, as well as attract one another, since most of the intermolecular energies vary inversely with the sixth power of the distance between molecules. Examples of the effect of *regularity* are given in Table 3-2.

The isotactic form is not always the most crystalline. In poly(vinyl alcohol), for example, the syndiotactic form crystallizes more readily than the isotactic because there are strong repulsive forces between adjacent hydroxyl groups [21] in the isotactic form.

TABLE 3-2
Effect of Regularity on Polymer Crystallinity

Irregularity	Polymer	Typical percent crystallinity
Copolymer	Linear polyethylene	70
	Isotactic polypropylene	70
	Linear random copolymer	None
Tacticity	Isotactic polypropylene	70
	Atactic	None
	<i>trans</i> -1,4-Polybutadiene	40
Cis-trans	<i>cis</i> -1,4-Polybutadiene	30 (at 0°C-long times)
	Random cis and trans	None
	Linear polyethylene	70
Linearity	Branched polyethylene	40

Examples of the effect of polarity are:

Nonpolar	Polypropylene (atactic), noncrystalline
Polar	Poly(vinyl alcohol) (atactic), somewhat crystalline
Very polar	Polyamide (nylon 6), very crystalline

3-8 TRANSITION TEMPERATURES

For most polymers, there is a single temperature (in an experiment with a given time scale) at which the onset of segmental motion occurs; it is termed the glass transition temperature, T_g . Similarly, for those polymers which crystallize to any extent, there is a single melting temperature, T_m (which does depend to some extent on molecular weight). However, in both the amorphous and crystalline phases, additional rearrangements or relaxation processes can occur. Usually these do not result in obvious changes in properties. Sometimes they are observed as peaks in damping versus temperature plots resulting from oscillatory deformations (see Secs. 8-7 and 8-9).

Since crystallinity depends strongly on regularity, but T_g does not, it is conceivable that some copolymers might form glasses before they can crystallize. This is the case for ethylene-propylene copolymers of roughly equimolar proportions. When polymerized by a catalyst that gives highly crystalline, linear polyethylene or highly crystalline, isotactic polypropylene, a mixture of the monomers gives an amorphous, rubbery material that does not crystallize but only forms a glass on cooling to about -60°C . Another example is shown in Fig. 3-14. Here, adding about 20% of

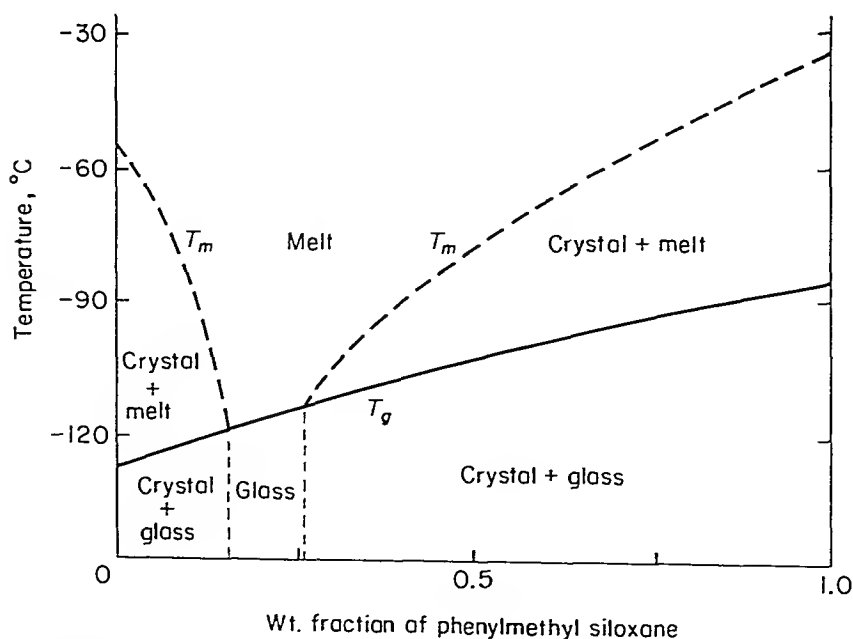


FIGURE 3-14

Loss of crystallinity by copolymerization of phenylmethyl siloxane with dimethyl siloxane [22].

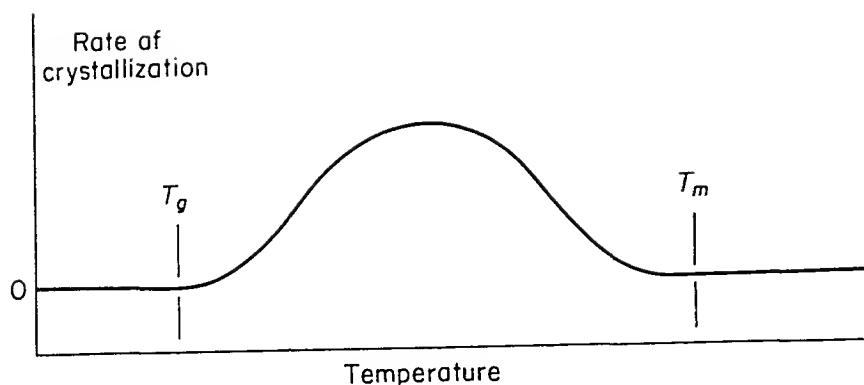


FIGURE 3-15

Rate of crystallization rises to a maximum between T_g and T_m .

phenylmethylsilanol is sufficient to destroy the crystallinity of polydimethylsilanol without substantially raising the T_g .

It is obvious from the foregoing that, for partially crystalline materials, T_m is always greater than T_g and that the difference is a maximum for homopolymers. An examination of these parameters for many homopolymers leads to the generalization that [23]

$$1.4 < \frac{T_m}{T_g} < 2.0 \quad (3-4)$$

The ratio generally is higher for symmetrical polymers such as poly(vinylidene chloride) than it is for unsymmetrical polymers such as isotactic polypropylene. Some other generalizations can be made in light of what has been said so far. The rate of polymer crystallization increases as the temperature is lowered from T_m . However, no crystallization takes place effectively below T_g . Consequently, the maximum rate of crystallization occurs at a temperature between T_m and T_g (Fig. 3-15). If a sample of molten polymer is quenched rapidly to a temperature below T_g , a metastable glass may be obtained. Warming the sample just above T_g can increase crystallinity, making the sample stiffer. In the interesting situation that then arises, a glassy polymer is heated, becoming progressively softer as the temperature increases, suddenly stiffens, and then softens again as the T_m is approached (Fig. 3-16).

The *melting point* T_m of a polymer usually is more properly termed a melting range, because a single specimen consists of more than one molecular weight and more than one crystal size. Decreasing either molecular weight or crystal size lowers T_m somewhat. Besides the disappearance of opacity (seen by transmitted light) and polymer orientation (seen by transmitted polarized light), T_m can be characterized by the abrupt change in specific volume V that occurs (a first-order transition) (Fig. 3-17). Chain stiffness also has an effect on T_m . Two linear, nonpolar polymers are linear polyethylene and isotactic polystyrene. The bulky phenyl groups hinder rotation around single bonds in the polystyrene backbone. Since this rotation is the source of chain flexibility, it is not surprising that polystyrene is much stiffer than polyethylene. This shows up in melting points: polystyrene, $T_m = 230^\circ\text{C}$; polyethylene,

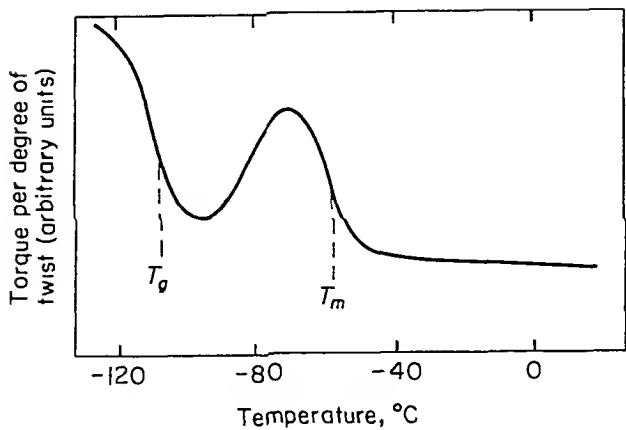


FIGURE 3-16
Quenched sample of silicone copolymer being heated from below T_g . Recrystallization between T_g and T_m increases stiffness, which then disappears when T_m is exceeded [22].

$T_m = 137^\circ\text{C}$. Qualitatively, one can picture the effect of stiffness by comparing (1) the peeling of a leather strap from a wall to which it is nailed with (2) the peeling of a stiff wooden board, also nailed. In the first, nails are stressed sequentially. In the second, all nails are stressed simultaneously. The molecular analogy for a nail is the intermolecular bond. Some typical values for T_m are summarized in Table 3-1.

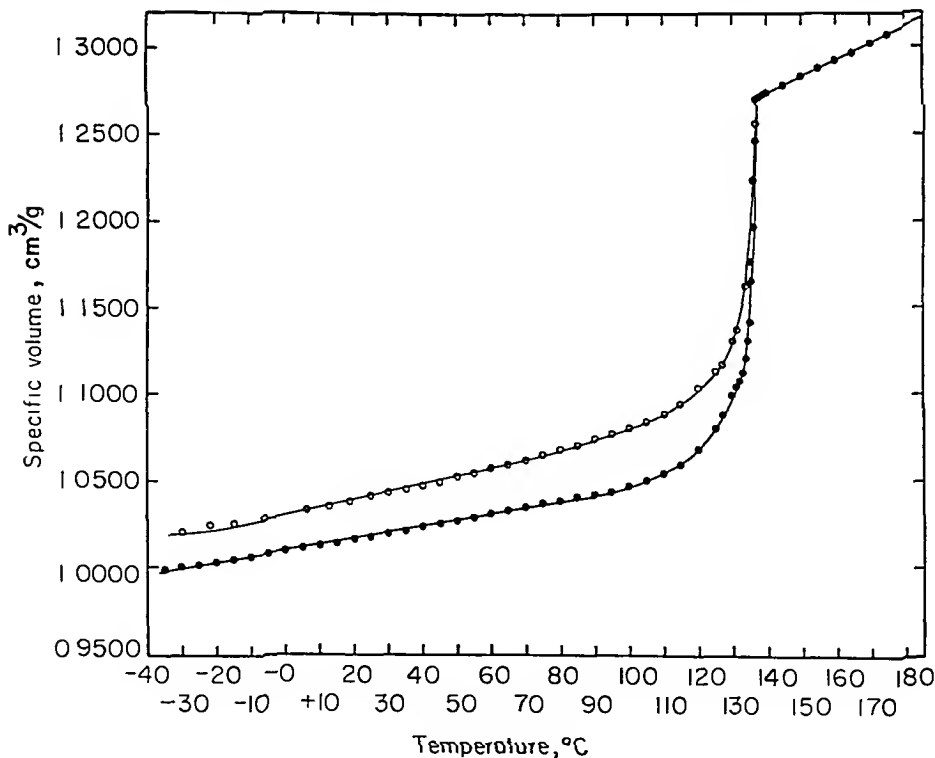


FIGURE 3-17
Specific volume-temperature relations for linear polyethylene (Marlex 50). Specimen slowly cooled from melt to room temperature prior to experiment (o) and specimen crystallized at 130°C for 40 days and then cooled to room temperature prior to experiment (●) [24].

Adding a solvent to a polymer decreases T_m in a manner predictable by the equation [25]

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u} \frac{V_u}{V_1} (v_1 - \chi v_1^2) \quad (3-5)$$

where V_u is the molar volume of the polymer repeat unit, ΔH_u is the heat of fusion per polymer repeat unit, V_1 is the molar volume of the solvent, v_1 is the volume fraction of the solvent, χ is the polymer-solvent interaction parameter, R is the gas constant, and T_m^0 is the melting point of the pure polymer (see Fig. 3-18, Table 3-3). Most of the time, the depression of T_m by a small amount of solvent is modest. For example, consider three volumes of polychloroprene, $(\text{CH}_2-\text{CCl}=\text{CH}-\text{CH}_2)_n$, diluted with one volume of a good solvent for which $V_1 = V_u$ and $\chi = 0.4$. From Table 3-3, $T_m^0 = 80^\circ\text{C}$ and $\Delta H_u = 2000$.

$$\frac{1}{T_m} - \frac{1}{353 \text{ K}} = \frac{1.987}{2000 \text{ K}} (0.25 - 0.4 \times 0.25^2)$$

$$T_m = 327 \text{ K} = 54^\circ\text{C}$$

Imposing a tensile strain on a polymer will cause a temporary orientation of chains in the direction of stress. Since this is a state of greater order, it represents a state of lower entropy, and therefore of higher free energy. An important consequence

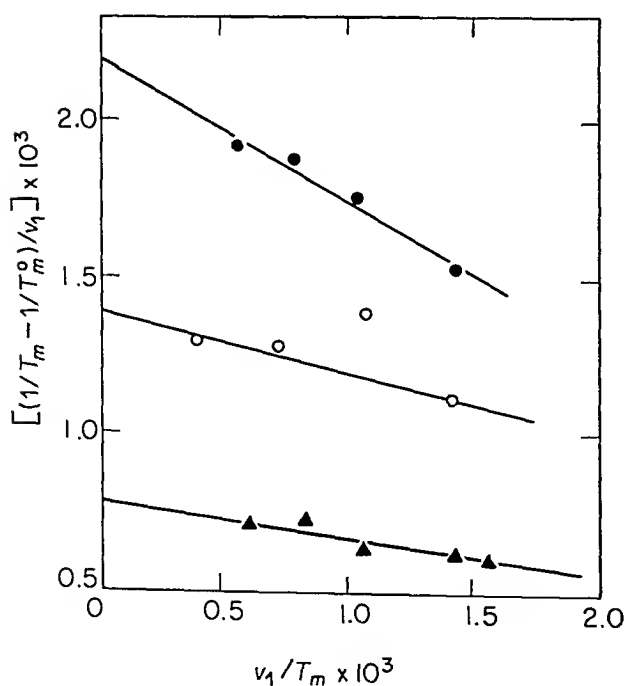


FIGURE 3-18

Temperature reduction as $(1/T_m - 1/T_m^0)/v_1$ plotted against v_1/T_m for cellulose tributyrate mixed with hydroquinone monomethyl ether (o), dimethyl phthalate (•), and ethyl laurate (▲) [26]. Linearity would not be greatly affected by replacing v_1/T_m by v_1 .

TABLE 3-3
Heat of Fusion of Selected Polymers [25]

	$T_m, ^\circ\text{C}$	$\Delta H_u, \text{cal/mol}^*$
Polyethylene, $(\text{CH}_2)_n$	137.5	960
<i>cis</i> -1,4-Polyisoprene	28	1050
<i>trans</i> -1,4-Polyisoprene	74	3040
<i>trans</i> -1,4-Polychloroprene	80	2000
Poly(vinyl fluoride)	197	1800
Cellulose tributyrate	207	3000
Poly(ethylene oxide)	66	1980
Poly(methylene oxide)	180	1590

*1 cal = 4.185 J.

is that the melting temperature of crystals formed under stress will be higher than when unstressed. Careful measurements in which T_m is extrapolated to a limiting value for perfect crystallites have been made (Fig. 3-19). The available theories are unsatisfactory in that they generally do not fit the observed T_m for unstressed polymer, although they can be used to correlate the changes in T_m at finite elongations.

A sizable increase in density with crystallization is characteristic of almost all materials. Only water, bismuth, and a few polymers are exceptions. The density of

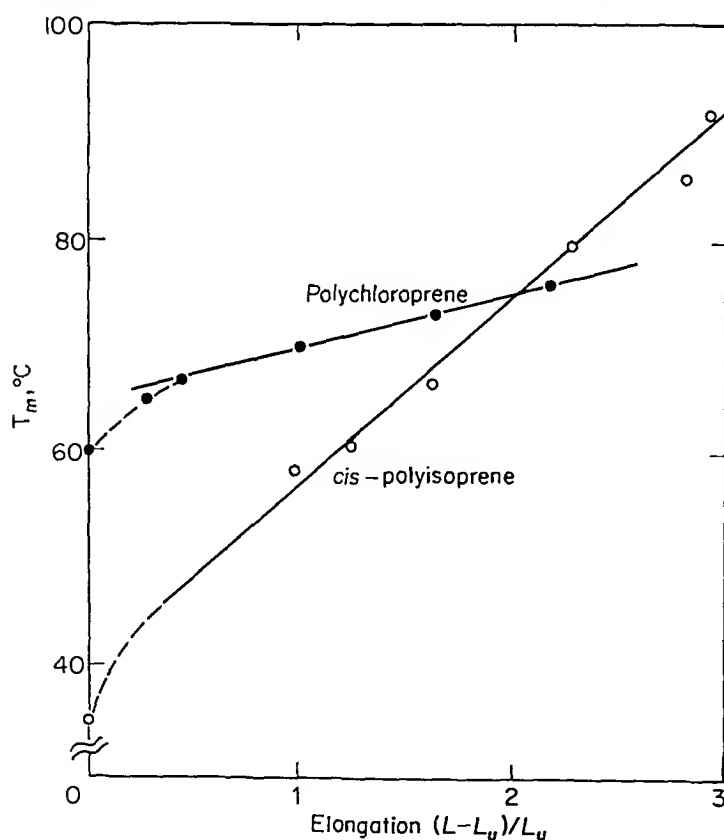


FIGURE 3-19

Strain-induced crystallization. L_u is the unstretched length [27].

perfectly crystalline materials can be derived from x-ray measurements. The amorphous material is easily measured above its melting point and the density extrapolated to lower temperatures. Knowing these densities at any temperature together with the actual density of a sample gives a convenient estimate of the degree of crystallinity:

$$\text{Percent crystallinity} = \frac{\text{sample density} - \text{amorphous density}}{\text{perfect crystal density} - \text{amorphous density}} \times 100 \quad (3-5)$$

Because chain atoms are involved in chain folding and in chain ends, it has been argued that even a single crystal could not be 100% crystalline on the basis described.

It should be obvious that characterization of a partly crystalline polymer is much more complex than mere specification of the fraction that is crystalline. Some factors that need to be taken into account have been listed by Magill [2] as:

1. crystallite size, crystallite distribution, and crystallite perfection
2. constraints on amorphous regions (matrix) that perturb it from its truly disordered condition
3. defects or distortions in the paracrystalline sense
4. presence of voids and surface stresses
5. polymer chain chemistry, where induced chain irregularities prevent the system from attaining its lowest energy state
6. transient and permanent entanglements in the amorphous regions
7. inherent strains that give rise to nonrandom states
8. chain length and chain ends
9. nature of interzonal or surface layer with distance
10. distribution of spherulite sizes
11. the relative sequence lengths for a block copolymer

PROBLEMS

- 3-1. When a saturated paraffin such as polymethylene $(\text{CH}_2)_n$ is chlorinated, chlorine replaces hydrogen at random. Invariably, small amounts of chlorine (10 to 50 wt % Cl) cause a lowering of softening point. Large amounts (*ca.* 70%) raise the softening point. Rationalize on the basis of intermolecular forces.
- 3-2. Polymers that are oriented on stretching may crystallize, since the molecules are then able to fit into a lattice more easily. How does this help explain why a rubber band heats up on stretching to near its breaking point? (Try this by holding a rubber band to your lips and suddenly stretching.)
- 3-3. Copolymers of monomers A and B have the following stiffening temperatures:

Weight fraction of B	Stiffening temperature, °C
0.00	60
0.10	36
<u>0.15</u>	<u>20.5</u>
0.25	-8.0
0.35	-3.0
<u>0.50</u>	<u>+5.0</u>

Estimate T_g for homopolymers of B and of A. Explain your assumptions.

- 3-4. For the polyethylene of Fig. 3-17 (lower curve), calculate the fraction of crystalline material at 20°C assuming the coefficient of expansion for amorphous material is the same above and below T_m and that the density of perfect crystal can be obtained from Fig. 3-10.
- 3-5. Compare graphically the temperatures of Table 3-1 with Eq. (3-4). Also plot T_m and T_g versus δ_2 . Explain extraordinary points.
- 3-6. From the data of Fig. 3-4, calculate the ratio of T_g for tritolyl phosphate to that for dioctyl sebacate. Is a T_g for dioctyl sebacate based on Eq. (3-2) or (3-3) realistic?
- 3-7. What is wrong with describing a sample of polyisobutylene as "predominantly cis" or "syndiotactic"?
- 3-8. The following data are obtained when linear polyethylene is mixed with α -chloronaphthalene [28].

$T_m, ^\circ\text{C}$	v_1 , vol. frac. of solvent
137.5	0.00
134.5	0.06
131	0.16
125	0.32
120	0.52
115	0.75
110	0.95

Densities of amorphous polyethylene and solvent are approximately 0.8 and 1.1 g/cm³, respectively. Estimate the heat of fusion of polyethylene and the polymer-solvent interaction parameter.

- 3-9. What is the repeat distance between pendant methyl groups that form a row in the H₃1 helix of isotactic polypropylene? What is the analogous distance in the H₂1 helix of syndiotactic polypropylene?
- 3-10. When held at a constant temperature, spherulites grow at a constant radial velocity. Crystallization rate may be studied by following the overall volume of a large sample containing many spherulites, each growing from a separate nucleus. Derive a formula for the change in density ρ with time t for a sample in which no new nuclei are formed after crystallization starts and in which the constant radial growth rate is $(dr/dt)_0$. Assume that we follow the density only during the time in which spherulites do not grow large enough to touch each other. Let densities of crystalline and amorphous polymer be ρ_c and ρ_a , respectively. For a general treatment of this problem, refer to Chap. 8 in Mandelkern's book (see general references for this chapter).
- 3-11. What melting temperature can be expected for poly(ethylene oxide) mixed with water when the volume fraction of solvent is 0.01, 0.02, and 0.05? The density of crystalline polymer is 1.33 g/cm³ and $\chi = 0.45$. See Table 3-3 for additional data.
- 3-12. The T_g of nylon 66 is lowered by water or methanol. Using Eq. (3-3), estimate T_g for the two liquids assuming that the temperature at which $E' = 2.0$ GPa is near T_g (Fig. 8-18).
- 3-13. How much plasticizer with $T_g = -80^\circ\text{C}$ would have to be added to a film of nylon 66 in order for T_g to be 25°C? If $V_1 = 200$ cm³/mol and $\chi = 0.40$, what would be the effect on T_m of this amount of plasticizer? Data: $\Delta H_u = 46.8$ cal/g, $\rho = 1.088$ g/cm³, $T_m = 265^\circ\text{C}$, $T_g = 50^\circ\text{C}$.

- 3-14. Two copolymers of ethylene ($\text{CH}_2=\text{CH}_2$) and propylene ($\text{CH}_2=\text{CHCH}_3$) have the same ratio of monomers. However, one is rubbery at room temperature and does not stiffen until the temperature is lowered to about -70°C , while the other is rather stiff, tough, and opaque at room temperature. Explain the difference.
- 3-15. What kind of isomerism might you expect in polymers of 1-butene ($\text{CH}_2=\text{CHCH}_2\text{CH}_3$)? Which form is likely to be least crystalline? What kind of isomerism do you expect in 1,4 polymerization of chloroprene ($\text{CH}_2=\text{CClCH}=\text{CH}_2$)? Which isomer should be most crystalline?
- 3-16. Why does an injection-molded polystyrene protractor show a complicated pattern when viewed in polarized light?
- 3-17. Polycaprolactone has $T_g = -60^\circ\text{C}$ and $T_m = +60^\circ\text{C}$. In the study of biodegradability at 25°C it would be desirable to vary the degree of crystallinity holding all other variables constant. Why is this difficult with polycaprolactone? Why should it be easier with poly(ethylene terephthalate), which has $T_g = +60^\circ\text{C}$ and $T_m = 250^\circ\text{C}$?

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4

POLYMER FORMATION

4-1 POLYMERIZATION REACTIONS

Polymerization is the process of joining together small molecules by covalent bonds. Around the turn of the century, chemists were reluctant to accept the idea of rubber, starch, and cotton as long, linear chains connected by covalent bonds. A popular alternative was the idea of an "associated colloidal" structure. As a matter of fact, some small molecules do exhibit such behavior. The extraordinary thickening power of aluminum disoaps in organic solvents is due to the formation of macroscopic structures from small molecules. However, the effective molecular weight of such a structure varies with concentration and temperature, whereas the molecular weight of true polymers with covalent links does not.

The reactions by which some complex, naturally occurring macromolecules are formed are not completely understood. Even *cis*-polyisoprene, natural rubber, which can be made in a single step from isoprene in the laboratory, is synthesized by a rather complex series of reactions in the rubber tree.

The ultimate starting materials for synthetic polymers are few in number. Petroleum, natural gas, coal tar, and cellulose are the main sources. In recent years ethylene and propylene from natural gas and petroleum refining have been used as a starting point for a variety of monomers.

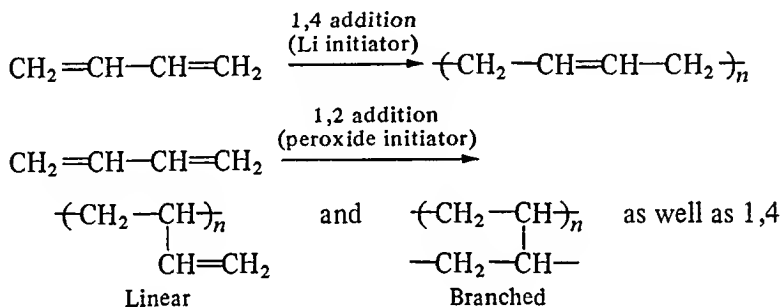
The process of building up polymers from simple repeating units (monomers) can proceed with many variations. We can classify some of these as follows:

1. By the number of bonds each monomer can form in the reaction used, the functionality.
2. By the kinetic scheme governing the polymerization reaction, chain vs. stepwise reactions.
3. By the chemical reaction used to produce new bonds, ethenic addition, esterification, amidation, ester interchange, etc.

4. By the number of monomers used to give homopolymer, copolymer, terpolymer, etc.
5. By the physical arrangement, bulk, solution, suspension, or emulsion system.

4-2 FUNCTIONALITY

Monomer can be converted to polymer by any reaction that creates new bonds. Fundamental to any polymerization scheme is the number of bonds that a given monomer can form. Carothers defined this number of bonds as the *functionality* of a monomer in a given reaction. Examples are given in Table 4-1. It should be obvious that a functionality of two can lead to linear structure. The necessity for specifying the reaction is emphasized by a monomer like butadiene, which can react in several ways:



4-3 KINETIC SCHEMES

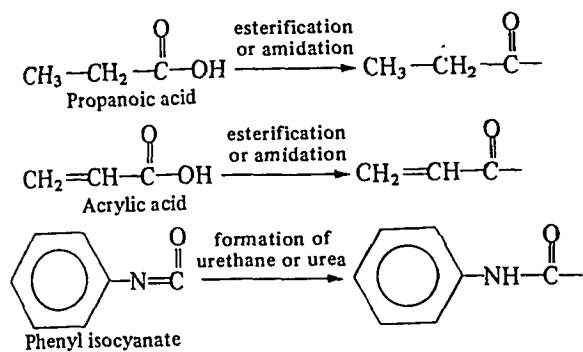
We can envision two extremes of simplified behavior in the conversion of monomer to polymer. In a typical *stepwise polymerization*, each polymer formed can react further with monomer or other polymers. Each dimer, trimer, etc., is just as reactive as monomer. In a typical *chain polymerization* each polymer is formed in a comparatively short time, and then is "dead" and remains unchanged by the reaction of remaining monomer. Growing chains can add monomer, but neither monomer itself nor "dead" polymer can add monomer. Monomer, growing polymer, and "dead" polymer are quite different from one another in reactivity. Imagine a system of 100 monomer units (Fig. 4-1). We carry out a reaction that consumes 50 monomer units, i.e., half the original charge is unchanged while the other half is altered by having formed covalent bonds with other units.

The distribution of molecular weights is quite different for the two cases (Fig. 4-2). Further reaction of the stepwise polymer will gradually change the distribution toward higher values of x , the number of monomer units in a polymer. Further reaction in the chain polymer system will diminish the monomer concentration, but will also increase the amount of polymer at high values of x .

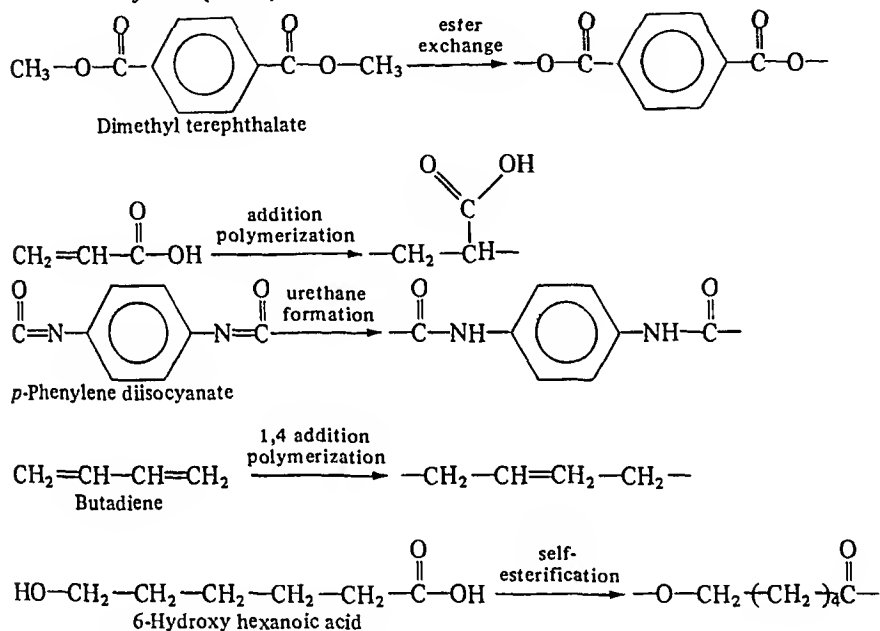
While these extremely simplified cases are met in practice, some very important exceptions occur that show the need for caution in making generalizations.

TABLE 4-1
Functionality and Structure

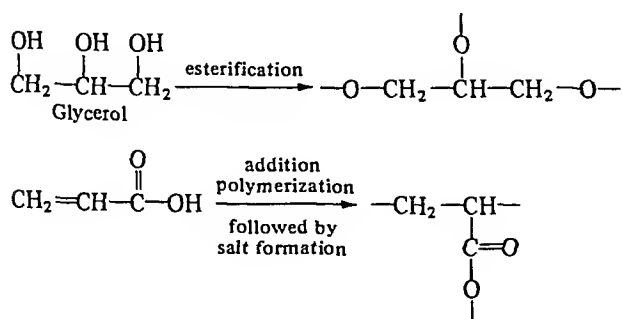
1. Functionality of 1 (A—)



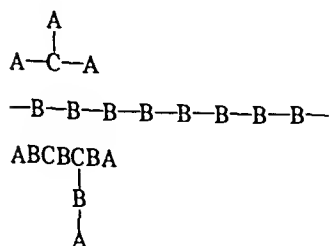
2. Functionality of 2 (—B—)



3. Functionality of 3 (—C—)



4. Structures



Example:

A = propanoic acid

C = glycerol

B = acrylic acid

A = ethanol

B = dimethyl terephthalate

C = glycerol

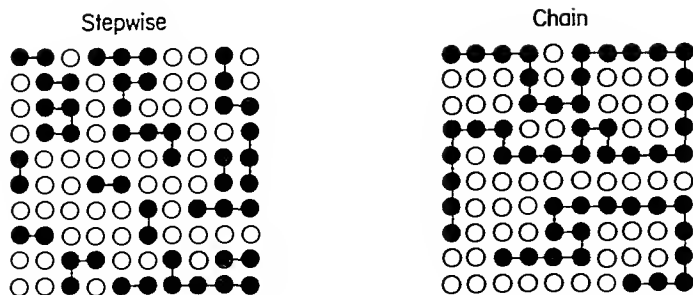


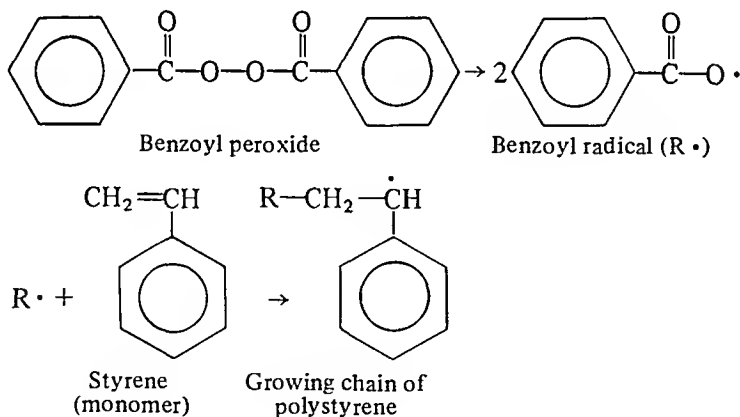
FIGURE 4-1

In stepwise polymerization, each polymer ($\text{---}\bullet_n$) is as reactive as monomer ($\circ$). In chain polymerization, each polymer is dead and can no longer react with monomer.

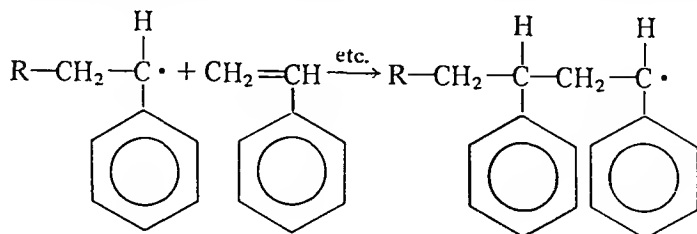
4-4 CHAIN POLYMERIZATION

Ethenic polymerization is an economically important class whose kinetics typify chain polymerization [1]. The terms “vinyl,” “olefin,” or “addition polymerization” are often used, although they are more restrictive. Usually three stages are essential to the formation of a useful high polymer:

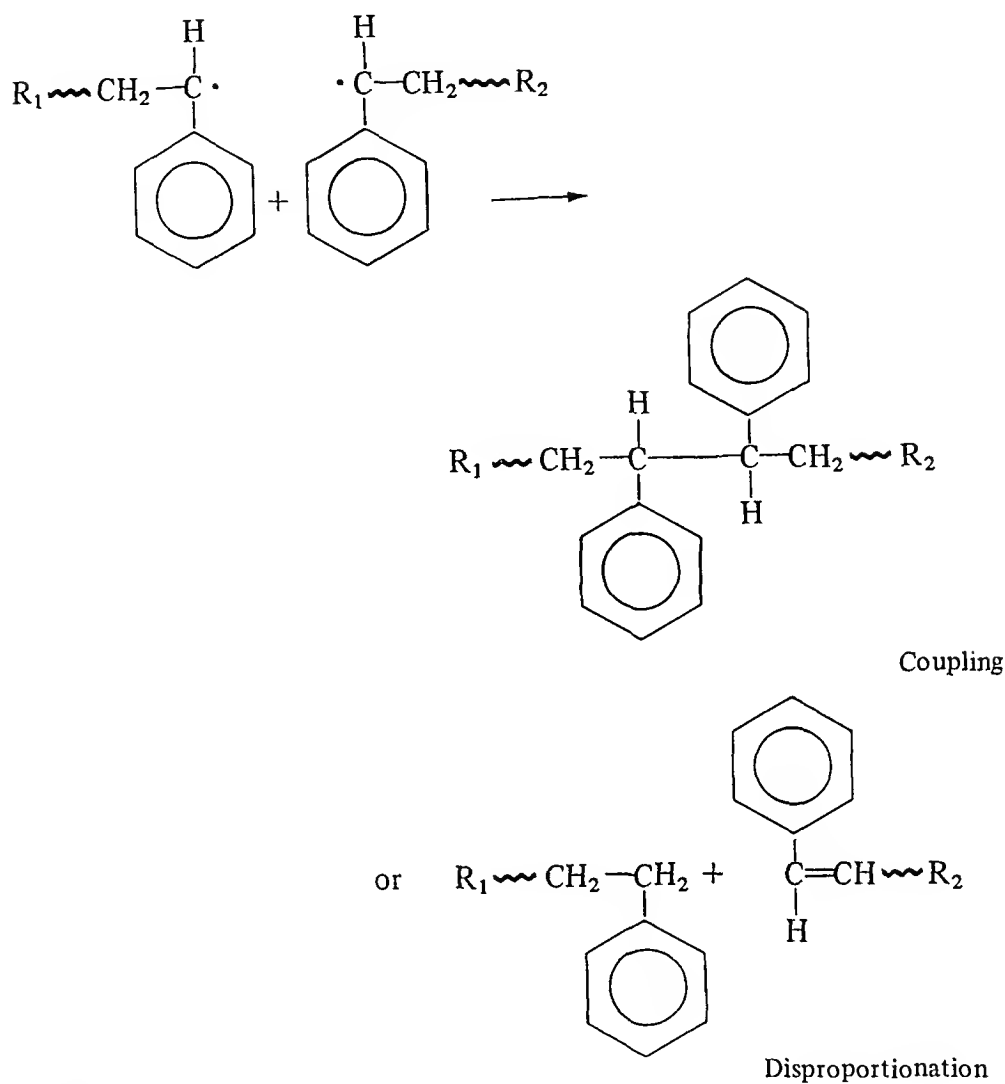
Initiation is the creation of an “active” center such as a free-radical, carbanion, or carbonium ion. For example, radicals from the thermal dissociation of benzoyl peroxide can initiate the chain polymerization of styrene.



Propagation is the addition of more monomer to growing chain end—usually very rapidly (for example, mol wt of 10^7 in 0.1 s) to final molecular weight.



Termination is the disappearance of an "active" center.



Other propagating systems are described in Sec. 4-5.

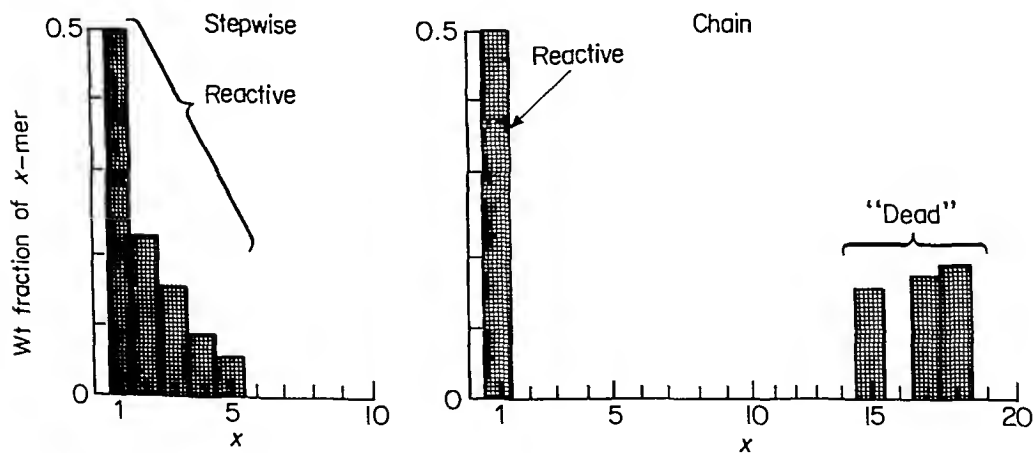
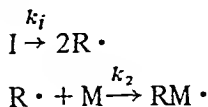


FIGURE 4-2

Histograms of weight fraction vs. degree of polymerization (x) for the examples of Fig. 4-1.

A shorthand notation for these reactions is:

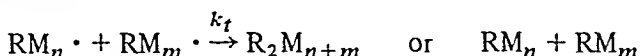
Initiation:



Propagation:



Termination:



As seen here, each reaction is characterized by a rate constant. It is a cornerstone of polymerization theory that the reactivity of a growing polymer chain depends almost completely on the last unit added and not on previously added units or on the length of the chain. Therefore k_p is the same for a chain of any length.

The kinetic model consistent with this mechanism is simple, provided the following assumptions are valid (quantities in brackets are concentrations, e.g., moles per liter).

1. Reaction proceeds slowly enough that a steady state is reached, where the radical population does not change rapidly with time

$$\left(\frac{d[R \cdot]}{dt} \quad \text{and} \quad \frac{d[M \cdot]}{dt} = 0 \right)$$

Material balances then give

$$2k_i[I] - k_2[R \cdot][M] = \frac{d[R \cdot]}{dt} = 0 \quad (4-1)$$

$$k_2[R \cdot][M] - 2k_t[M \cdot]^2 = \frac{d[M \cdot]}{dt} = 0 \quad (4-2)$$

2. The propagation reaction occurs so much more often than the others that it is effectively the only consumer of monomer.

$$\text{Rate of polymerization} = R_p = -\frac{d[M]}{dt} = k_p[M \cdot][M] \quad (4-3)$$

Under these conditions, we get first-order dependence on monomer and half-order dependence on initiator:

$$R_p = k_p \left(\frac{k_i}{k_t} \right)^{0.5} [M] [I]^{0.5} \quad (4-4)$$

If only a certain fraction f of initiator fragments can successfully react with monomer, we have

$$R_p = k_p \left(\frac{fk_i}{k_t} \right)^{0.5} [M] [I]^{0.5} \quad (4-5)$$

Often in experimental studies the monomer concentration is measured as a function of time for various starting concentrations of monomer and initiator and at various temperatures. When making high-molecular-weight polymer, relatively few initiator molecules will be consumed compared to the number of monomer molecules. If $[I]$ can be assumed to be essentially constant, Eq. (4-4) can be integrated to give

$$2.303 \log_{10} \frac{[M]_0}{[M]} = k_p \left(\frac{k_i}{k_t} \right)^{0.5} [I]^{0.5} t \quad (4-6)$$

A semilog plot of concentration vs. time should give a line with an intersection for $t = 0$ at the initial concentration and a slope related to the rate constants and initiator concentration (Fig. 4-3). For various reasons, such as diffusion-controlled reaction or more complex mechanisms, the experimental order for a polymerization may be more or less than one. We shall see later (Sec. 5-6) that an emulsion polymerization may be zero order in overall monomer concentration. If conversion is followed only to 50%

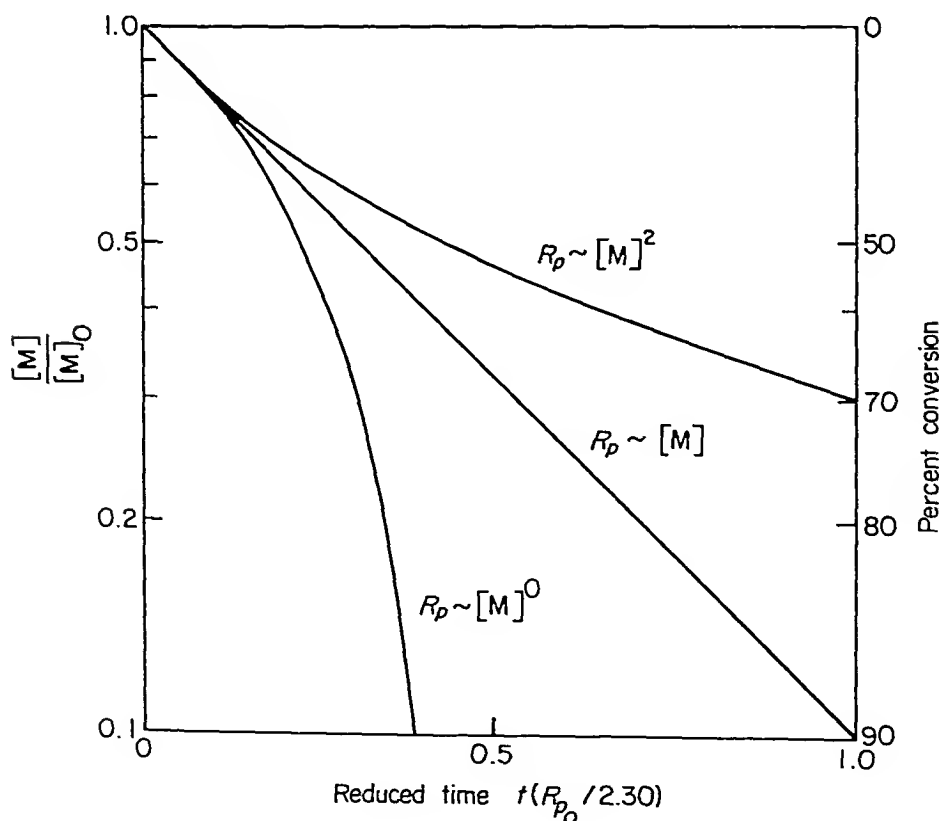


FIGURE 4-3

Concentration-time plots for three polymerizations having the same rate of monomer consumption, initially R_{p0} , but having a rate that depends on monomer concentration to the zero, first, or second power.

conversion (Fig. 4-3) the slight curvature presented by zero to second-order reactions may not be readily seen. On the other hand, systematic errors in concentration analysis, heat transfer, or induction periods can produce curvature in such plots, which then relate to no fixed order. The deviations of many polymerizations from first-order kinetics (and half-order in initiator) often are a valuable clue to unraveling the sequence of reaction steps. Careful analysis and reasonable replication are essential. Another check on the order is to plot the polymerization rate, often the initial rate, against initial concentration of monomer and initiator (Fig. 4-4). The complication of simultaneous depletion of monomer and initiator is minimized here.

The individual rate constants in Eq. (4-4) or (4-5) are not determined by the experiments described so far. The initiation rate k_i can be evaluated from nonpolymerization studies. For many peroxides, the first-order decomposition constants have been evaluated in inert solvents. Usually the half-life $t_{1/2}$ is given as a function of temperature, and $t_{1/2} = 0.693/k_i$. Some typical values are given in Fig. 4-5. A complication in using these for k_i is that not every radical produced initiates a chain. To measure the effective number of radicals, it is necessary to carry out an actual polymerization or a reaction with a compound that is known to react in the same way as monomer but more easily analyzed. If k_i is known with confidence from one monomer reaction, it can be used in others in order to separate a value of $k_p/(k_t)^{0.5}$ for the individual monomer. Some of the latter are listed in Table 4-2. A further separation of k_p from k_t is more difficult, but it can be attained by several methods. One of these is intermittent photoinitiation, which gives a measure of chain growth rate [3]. Another method is emulsion polymerization with a known particle population (Sec. 5-6). Some experimentally derived values for k_p and k_t are given in Table 4-2.

The molecular weight that results from a chain polymerization with simple kinetics can be deduced from the scheme outlined so far. First, it is necessary to define the kinetic chain length and the degree of polymerization. The *kinetic chain-*

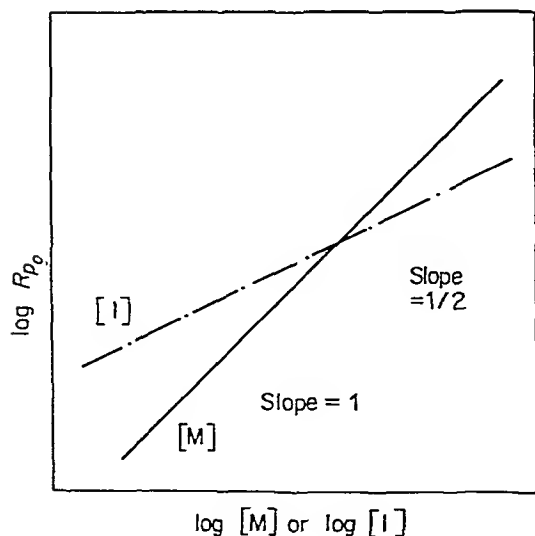


FIGURE 4-4

Expected correlation of initial rate R_{p0} with initial concentrations of initiator I or monomer M.

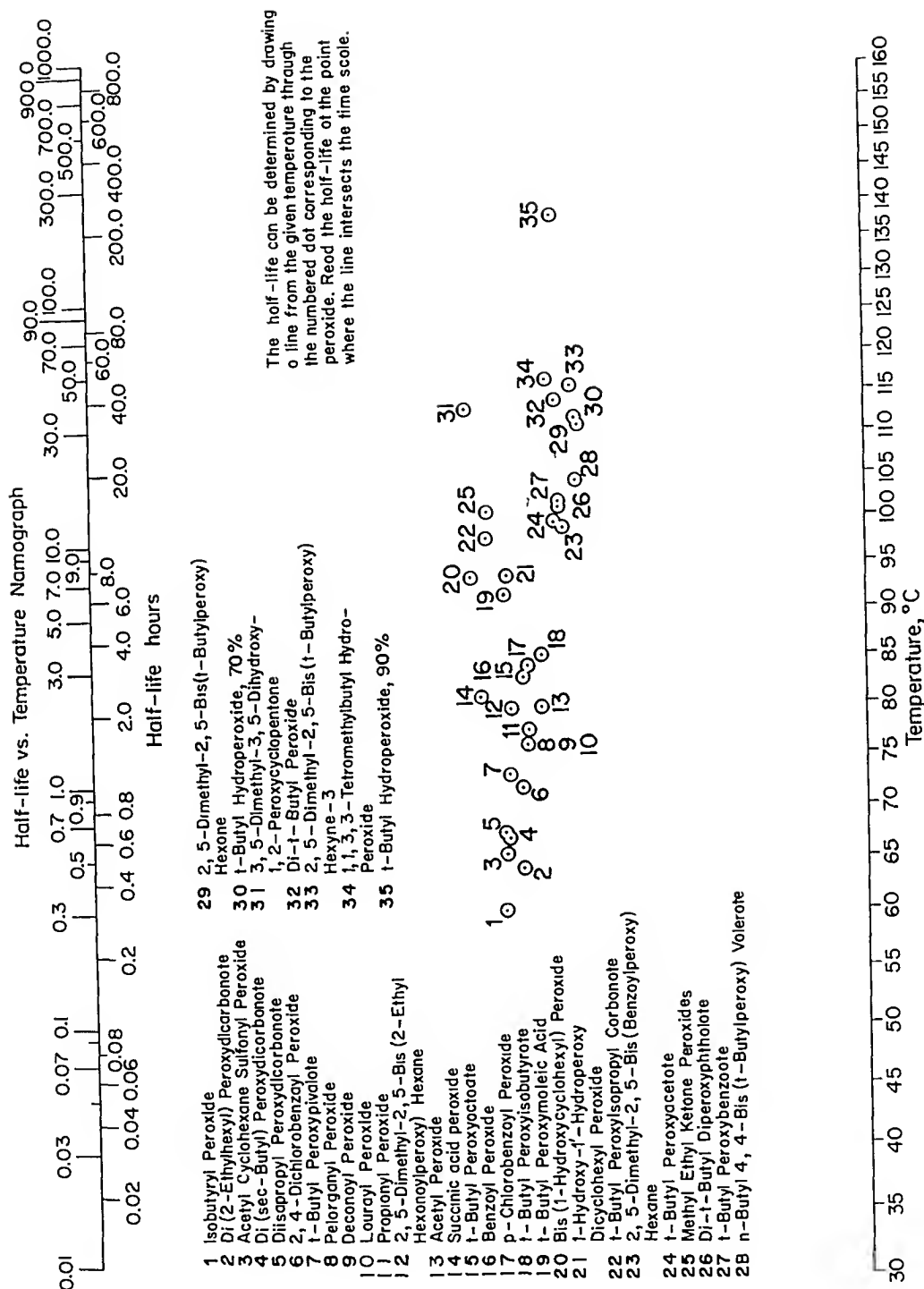


FIGURE 4-5
Thermal stability of organic peroxides as indicated by time for decomposition of 50% of original charge (half-life for first-order reaction) [2].

TABLE 4-2
Selected Propagation and Termination Rate Constants [4]

Monomer	Tem- pera- ture, °C	$k_p^2/k_t \times 10^3$, liters/mol·s	k_p , liters/mol·s	$k_t \times 10^{-6}$, liters/mol·s	E_p , kcal/mol	E_t , kcal/mol
Acrylamide	25	22,000	18,000	14.5		
Methyl acrylate	30	120	720	4.3	7	5
	60	460	2,090	9.5		
Methyl methacrylate	30	3.0	251	21	5	0.5
	60	10	515	25.5		
	80	21	800	30.5		
Styrene	50	0.38	209	115	7	2
Vinyl acetate	60	240	9,500	380	7	5

length ν_n is the number of monomer units converted per initiating radical, so that

$$\nu_n = \frac{\text{rate of monomer consumption}}{\text{—rate of radical formation}} = \frac{R_p}{2k_t[I]} \quad (4-7)$$

Using Eq. (4-5), we get

$$\nu_n = \frac{k_p}{2} (fk_t k_t)^{-0.5} [M] [I]^{-0.5} \quad (4-8)$$

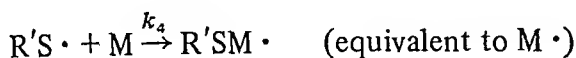
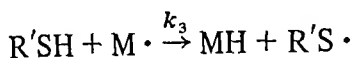
The number-average degree of polymerization $\bar{x}_n$ is

$$\bar{x}_n = \frac{\text{total monomer units in system that have reacted}}{\text{total molecules in system}} \quad (4-9)$$

It should be noted that, by convention, in stepwise polymerization, unreacted monomer is *included* in the numerator of Eq. (4-9). However, in chain polymerization, unreacted monomer usually is *not included*. Likewise, unreacted monomer molecules are counted in the denominator for stepwise polymerization but not for chain polymerization. The rationale for this is based on the usual discontinuity between monomer and polymer in chain polymerizations (Fig. 4-2). If termination is by disproportionation, $\bar{x}_n$ is the same as ν_n ; if by coupling, $\bar{x}_n = 2\nu_n$. Both mechanisms are important in practice. For example, styrene terminates almost exclusively by coupling, while methyl methacrylate typically terminates 58% by disproportionation and 42% by coupling [5]. As polymerization proceeds, ν_n , and therefore $\bar{x}_n$, will decrease because monomer is being consumed. The distribution of molecular weights being produced then is caused by the random nature of termination together with the constantly changing average molecular weight, since each "dead" polymer increment retains its initial molecular weight.

It often happens that $\bar{x}_n$ is much smaller than ν_n . A major reason for this is

chain transfer. For example, dodecyl mercaptan ($C_{12}H_{25}SH$ or $R'SH$) is widely used as a *chain transfer agent* where it is desirable to decrease molecular weight in radical polymerization. The agent enters the propagation scheme by giving up a proton to the growing radical chain, terminating it, but possibly initiating a new chain.



If $k_3 \cong k_4 \cong k_p$, the interposing of such an agent will not change ν_n , but it will decrease $\bar{x}_n$, since more than one dead polymer chain has been formed from one initiating fragment ($R \cdot$). In the commercial production of styrene-butadiene rubber, dodecyl mercaptan might be added at a ratio of 1 part of mercaptan to 200 parts of monomer, enough to reduce the average molecular weight several-fold. Of course, other species present during polymerization can act as chain transfer agents. Solvent, initiator, monomer, or polymer sometimes are involved. In the simple case of only one transfer reaction with constant k_3 and with k_4 large compared to k_3 , the rate of radical termination leading to new molecules is increased by the number of times the radical is transferred:

$$\text{Rate of molecule generation} = \Upsilon k_t [M \cdot]^2 + k_3 [R'SH] [M \cdot] \quad (4-10)$$

where Υ has a value of 1 if termination is by coupling and a value of 2 if termination is by disproportionation. Then the degree of polymerization becomes

$$x_n = \frac{k_p [M] [M \cdot]}{\text{rate of molecule generation}} \quad (4-11)$$

Rearranging and substituting (4-10) into (4-11):

$$(x_n)^{-1} = \frac{\Upsilon k_t [M \cdot]}{k_p [M]} + \frac{k_3 [R'SH]}{k_p [M]} \quad (4-12)$$

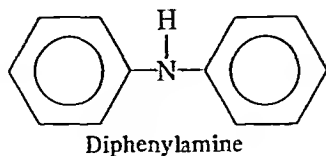
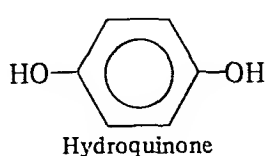
$$\text{or} \quad (x_n)^{-1} = (x_n)_0^{-1} + \frac{C_s [R'SH]}{[M]} \quad (4-13)$$

where $(x_n)_0$ is the number-average degree of polymerization that would occur in the absence of any chain transfer. A plot of $(x_n)^{-1}$ versus $[R'SH]/[M]$ should give a straight line with an intercept of $(x_n)_0^{-1}$ and a slope of C_s , the *chain transfer constant*. The chain transfer constant is specific for a given monomer and agent combination under particular conditions of solvent composition and temperature. In the more general case, chain transfer can take place between radical chains and many other species such as monomer, solvent, or even "dead" polymer. Any molecule from which a hydrogen atom can be abstracted to terminate one chain and to leave behind a radical of adding monomer is a possible chain transfer agent. A broader form of Eq. (4-13) for the general case is:

$$(x_n)^{-1} = (x_n)_0^{-1} + \sum \frac{C_i[A_i]}{[M]} \quad (4-14)$$

where C_i is the chain transfer constant for the agent A_i present in concentration $[A_i]$.

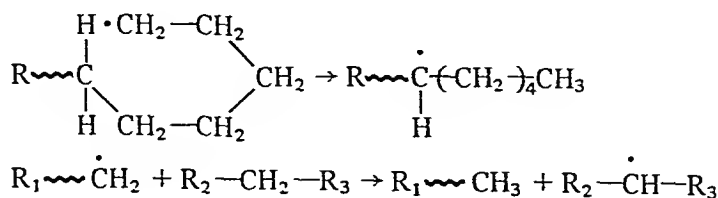
If $k_4 < k_p$, the overall rate will be decreased by chain transfer. This is "degradative" chain transfer. In fact, if k_4 is so small as to be negligible, chain transfer results in inhibition and the agent is a free-radical sink, or *inhibitor*. Almost all ethenic monomers are stored and shipped containing such a material to prevent adventitious polymerization. Hydroquinone and diphenylamine are compounds that at concentrations of 10 to 200 ppm are effective inhibitors.



The radicals that result from these compounds are unreactive toward monomer. Before a polymerization is carried out, inhibitors can be removed by distillation or by extraction (e.g., dilute caustic in the case of hydroquinone in a water-insoluble monomer), or they can simply be overcome by an excess of initiator which "uses up" the inhibitor during an "induction period."

Dissolved oxygen in a polymer system often acts as an inhibitor by reacting with radicals to give stable species. The variable induction periods that result can be annoying. Free-radical polymerizations usually are carried out under an inert atmosphere for this reason. Some early workers sought to obviate the necessity for deaeration in commercial reactors by adding reducing agents to act as scavengers for oxygen. The greatly increased rates that resulted when this was done were later explained by the fact that, while oxygen scavenging was not very efficient, the reducing agent-oxidizing initiator combination produced radicals much faster than the oxidizing agent could by itself. Such *redox couples* now are commonly employed to obtain fast rates at low temperatures by "reduction-activation." For example, the initial rate of polymerization of acrylamide with oxidizing agent (persulfate) is increased sevenfold by a modest amount of reducing agent (thiosulfate) (Fig. 4-6).

In many systems a polymer can be dead to the usual addition of monomer, but alive in the sense that it can act by a different mechanism as a transfer agent. At high temperatures and pressures, growing polyethylene chains abstract protons from themselves ("backbiting") or from other dead polymer.



These two processes result in short and long branches, respectively, because each new radical can add to monomer. Monomer itself can be a chain transfer agent. It is

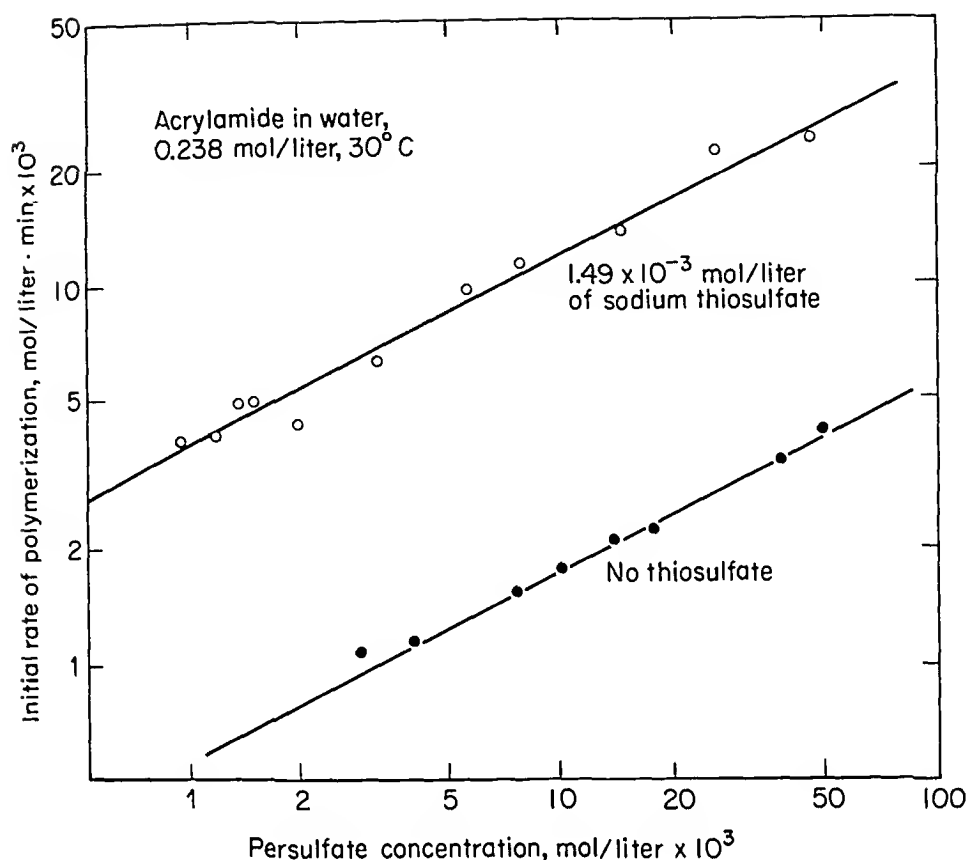
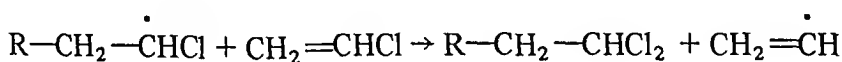


FIGURE 4-6

Increase in polymerization rate by addition of reducing agent, $\text{Na}_2\text{S}_2\text{O}_3$, to reaction initiated by $\text{K}_2\text{S}_2\text{O}_8$. Slope of log-log plot is $\frac{1}{2}$ in either case [6].

hard to tell whether vinyl chloride ($\text{CH}_2=\text{CHCl}$) terminates by coupling or by disproportionation, since most chains are terminated by having a growing radical abstract a chlorine atom from a monomer molecule.



The resultant radicals are not thought to initiate chains but rather to combine to form butadiene which subsequently copolymerizes with vinyl chloride [7].

The temperature dependence of the reaction rate constants k_i , k_p , etc., can be expressed as conventional Arrhenius equations:

$$k = A \exp \left(-\frac{E_a}{RT} \right) \quad (4-15)$$

where E_a is the *activation energy*, A is the *collision frequency factor*, R is the gas constant, and T is the absolute temperature. The temperature dependence of the overall polymerization rate R_p follows from Eq. (4-4):

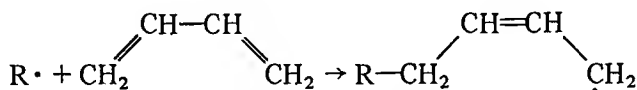
$$k_p \left(\frac{k_i}{k_t} \right)^{1/2} = A_p \left(\frac{A_i}{A_t} \right)^{1/2} \exp \left(\frac{E_t/2 - E_p - E_i/2}{RT} \right) \quad (4-16)$$

As an example, E_i for persulfate decomposition in water is 33.5 kcal/mol and $E_p - E_t/2$ for acrylamide polymerization is 1.5 kcal/mol. The calculated activation energy for R_p , 18.25 kcal/mol, is in fair agreement with a measured value of 16.9 kcal/mol [6].

Generally, the overall rate of polymerization increases with temperature. However, the variation of degree of polymerization with temperature follows from Eq. (4-8):

$$\frac{d(\ln x_n)}{dT} = \frac{d(\ln \nu_n)}{dT} = \frac{E_p - E_t/2 - E_i/2}{RT^2} \quad (4-17)$$

This discussion of chain polymerization has centered on free-radical polymerization of an ethenic monomer. Conjugated dienes such as 1,3-butadiene often polymerize as bifunctional monomers with 1,4 addition rather than as tetrafunctional monomers.



One double bond remains in the main chain for each monomer that reacts. Free-radical polymerization can also produce a 1,2 form of addition at the same time so that the polymer that results may be a kind of copolymer with some unsaturated side groups and perhaps even some network formation. Ionic and coordination-complex schemes of polymerization, described in the next section, not only can give almost all 1,4 addition with butadiene, but they also can be tailored to give all cis or all trans polymer as well. Free-radical polymerization usually gives a mixture of isomeric forms.

4-5 IONIC AND COORDINATION-COMPLEX POLYMERIZATIONS

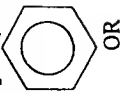
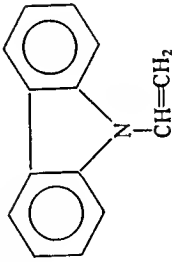
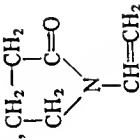
The reactivity of ethenic monomers to polymerization by radicals, ions, and complexing agents varies with the structure in a manner that can be correlated though not always quantitatively predicted. A convenient classification is that by Schildknecht (Table 4-3). It can be seen that for the vinyl monomer ($\text{CH}_2=\text{CHX}$), cationic initiation is favored when X is electron-donating and anionic when X is electron-withdrawing. In radical polymerization, the steric hindrance of the methyl group next to the double bond causes methacrylates, $\text{CH}_2=\text{C}(\text{CH}_3)(\text{COOR})$, to react much more slowly than the corresponding acrylates, $\text{CH}_2=\text{CH}(\text{COOR})$.

A major difference between radical polymerization and the various ionic methods is that, in the latter, the incoming monomer must fit between the growing chain end and an associated ion or complex. The growing radical chain, on the other hand, has no such impediment at the growing end.

Cationic Systems

Cationic polymerizations tend to be very rapid even at low temperatures. The polymerization of isobutylene with AlCl_3 or BF_3 is carried out commercially at -100°C

TABLE 4-3
Type of Chain Polymerization Suitable for Common Monomers [8]

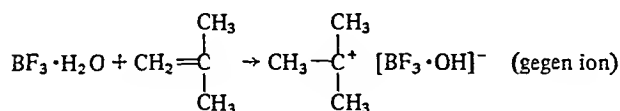
Cationic only	Free radical only	Anionic only
Isobutylene and derivatives, $\text{CH}_2=\text{C}(\text{CH}_3)_2$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{R}$ Alkyl vinyl ethers, $\text{CH}_2=\text{CHOR}$, and related ether types, $\text{CH}_2=\text{C}(\text{R})\text{OR}$, $\text{CH}_2=\text{C}(\text{OR})_2$, $\text{CH}_2\text{OCH}=\text{CHOCH}_3$ Coumarone, indene Derivatives of α-methylstyrene, $\text{CH}_2=\text{C}(\text{CH}_3)$ 	Halogenated vinyls, $\text{CH}_2=\text{CHX}$ $\text{CH}_2=\text{CX}_2$ $\text{CF}_2=\text{CFX}$ $\text{CF}_2=\text{CX}_2$ where X = halogen, hydrogen (but $\text{CH}_2=\text{CH}_2$ not included) Vinyl esters, $\text{CH}_2=\text{CHOCOR}$	Vinylidene cyanide, $\text{CH}_2=\text{C}(\text{CN})_2$, and related cyano derivatives, $\text{CH}_2=\text{C}(\text{CN})\text{Y}$, where Y = SO_2R, CF_3, COOR Nitroethylenes, $\text{CH}_2=\text{C}(\text{NO}_2)\text{R}$
Cationic or free radical <i>N</i>-vinylcarbazole, 	<i>N</i>-vinylpyrrolidone, $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})-\text{N}-\text{CH}_2-\text{CH}=\text{CH}_2$ 	Free radical or anionic Acrylic and methacrylic esters Vinylidene esters, $\text{CH}_2=\text{C}(\text{COOR})_2$ Derivatives of acrylonitrile, $\text{CH}_2=\text{C}(\text{CN})\text{CH}_2=\text{CRCONH}_2$
Ethylene, $\text{CH}_2=\text{CH}_2$; butadiene, $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$; styrene, $\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5$	Cationic, free radical, or anionic	
Coordination or supported metal oxide catalyst α-Olefins including ethylene, dienes, alkyl vinyl ethers		

(see Sec. 13-3). An estimate of the lifetime of a growing chain of isobutylene in this case is about 10^{-6} s [9]. This is much shorter than the usual lifetime of a free-radical chain such as vinyl acetate, which may be several seconds. If ionic catalysis is used in a heterogeneous system—e.g., insoluble catalyst, soluble monomer, and polymer—the rate of diffusion of monomer to and polymer from the surface may control the overall rate. In such cases, intensity of agitation, catalyst particle size, and viscosity of solvent can become very important. Usually a cocatalyst is involved. For example, water is the cocatalyst with BF_3 (Table 4.4), and it is $(\text{BF}_3 \cdot \text{OH})^-$ that forms the “gegen” ion (also called the “counter ion”) at the growing end of the chain. The fitting of the

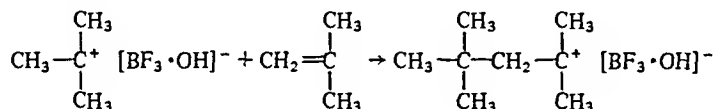
TABLE 4-4
Some Chain Polymerization Systems

Carbonium ion (cationic polymerization) [10]

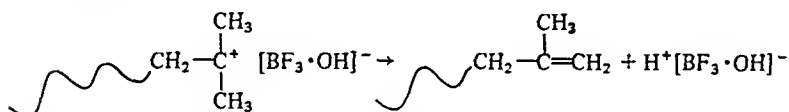
Initiation:



Propagation:

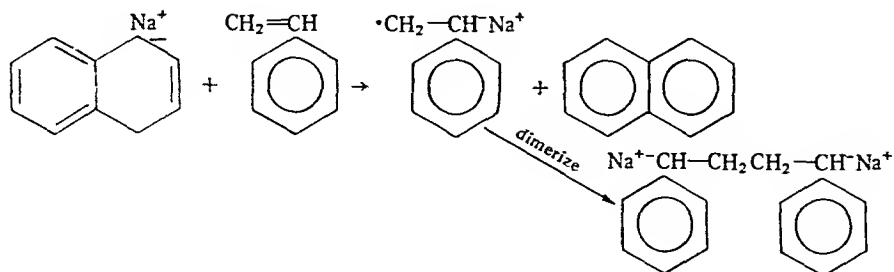


Termination:

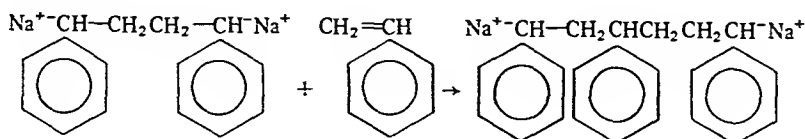


Carbanion (anionic polymerization) [11]

Initiation:



Propagation:



Termination:

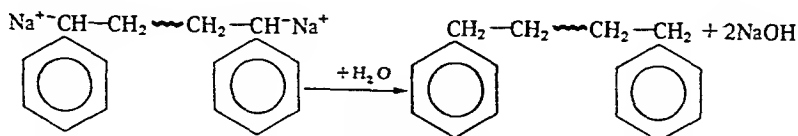
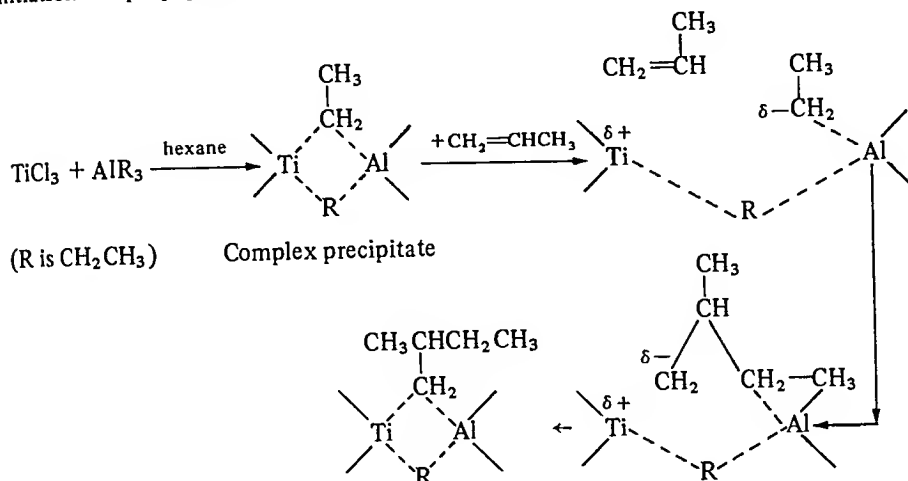


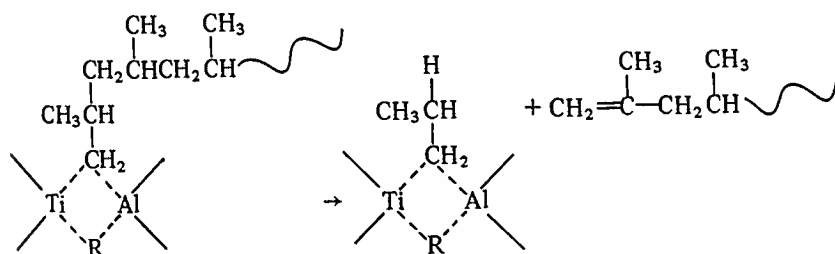
TABLE 4-4
Some Chain Polymerization Systems (Continued)

Coordination complex (Ziegler catalyst) [12]

Initiation and propagation:



Termination:

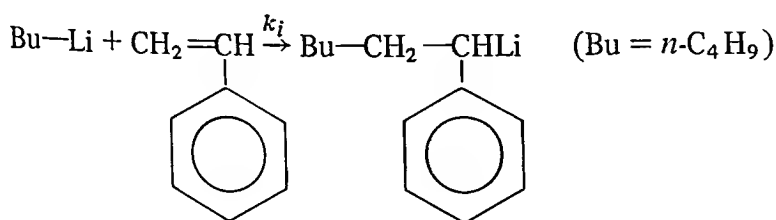


incoming monomer unit between chain and gegen ion can lead to stereoregularity, as when vinyl alkyl ethers are polymerized at very low temperatures [13].

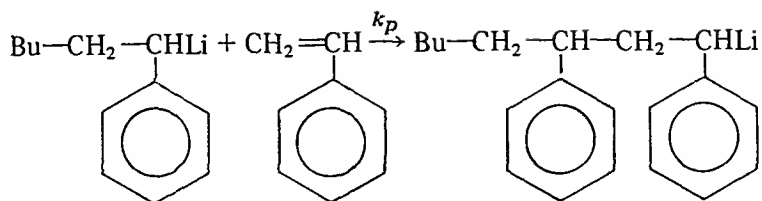
Anionic Systems

The particular usefulness of lithium alkyls has been with dienes to give *cis*-polyisoprene and *cis*-polybutadiene, although they can yield isotactic or atactic polymers of styrene and methyl methacrylate. It is a peculiarity of polymerizations with lithium alkyl that there is no termination step. The rate of polymerization depends on the amount of initiator and monomer present [14].

Initiation:



Propagation:



etc.

If the rate of initiation is much faster than the rate of propagation, each initiator should start one polymer chain. If all these start at time zero and grow to consume all the monomer, a narrow molecular-weight distribution (Poisson) results (see Sec. 6-2). The number-average degree of polymerization is given by $x_n = [M]/[I]$, where $[M]$ is the initial monomer concentration and $[I]$ is the initiator and, therefore, also the polymer concentration in moles per unit volume.

When butyl lithium is added to a monomer solution, the rate of initiation and propagation both depend on monomer concentration. If, however, the initiator is "seeded" by adding some monomer and then added to the remaining monomer, only the propagation step is observed. Under these circumstances the reaction is first order in monomer (Fig. 4-7), the straight line corresponding to

$$-\frac{d[M]}{dt} = k_p [M] [R_s] \quad (4-18)$$

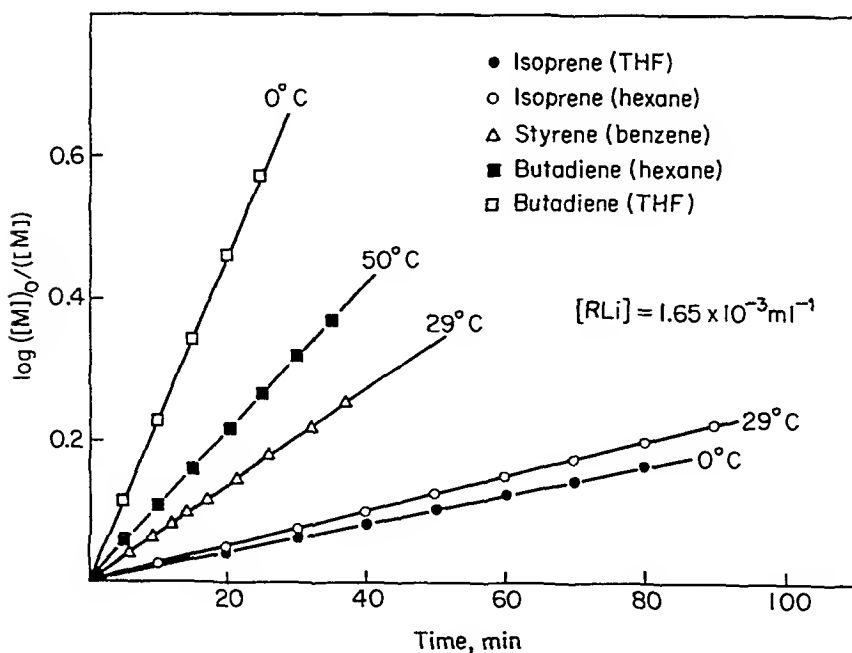


FIGURE 4-7

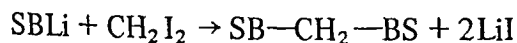
First-order rate plots for "seeded" butyl lithium polymerizations for monomers in benzene, hexane, or tetrahydrofuran [14].

$$\text{or } \ln \frac{[M]_0}{[M]} = k_p t [R_s] \quad (4-19)$$

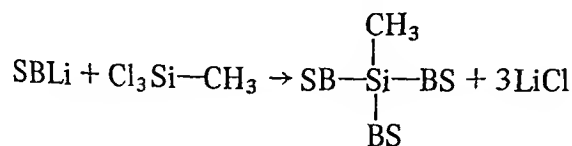
where $[M]$ is the monomer concentration at time t and $[M]_0$ at time $t = 0$ and $[R_s]$ is the concentration of growing polymer "seeds." The rate is proportional to the initiator concentration to the first power in tetrahydrofuran and to the second power in hydrocarbon solvents. This is because the lithium is associated in nonpolar solvents as a dimer. The final step is decomposition of the lithium alkyl by addition of water or alcohol. Various end groups can be attached to the chains by the reagent employed to "kill" the polymer. Since the polymer chains are "alive," a second monomer can be grown on a "seed" made from a different monomer.

Commercial copolymers based on styrene and butadiene have been prepared by this method. Both the random (both monomers present) and block (first one monomer added then the next) are available.

In one example [15], styrene (S) (60 g) in benzene (1400 g) is polymerized using 0.003 mol of *sec*-butyl lithium at 40°. Then isoprene (I) (450 g) is added and polymerized. Finally, an additional 60 g of styrene (S) is added and polymerized. Alcohol can then be added to cap the chain end and to precipitate the polymer. The chain thus made has the structure SIS where each letter in the abbreviation represents a *block* of monomer. A somewhat different block copolymer can be made by coupling together "living polymers" instead of merely capping them. Careful removal of moisture and air is necessary in either case. To make such a *radial* block copolymer, ordinary beverage bottles may be used [16]. Cyclohexane (40 cm³) is added followed by styrene (16 g) and *sec*-butyl lithium. After 40 min at 70°C in a tumbling rack, the bottle is cooled to 40°C and butadiene (B), (24 g) is added. At this point the orange-colored polystyryl anion is converted to the colorless polybutadienyl anion. Another hour at 70° gives essentially complete conversion. The final step is to add a coupling agent that will join the living polymers together. If a difunctional agent such as methylene iodide is used, a linear block copolymer is formed.

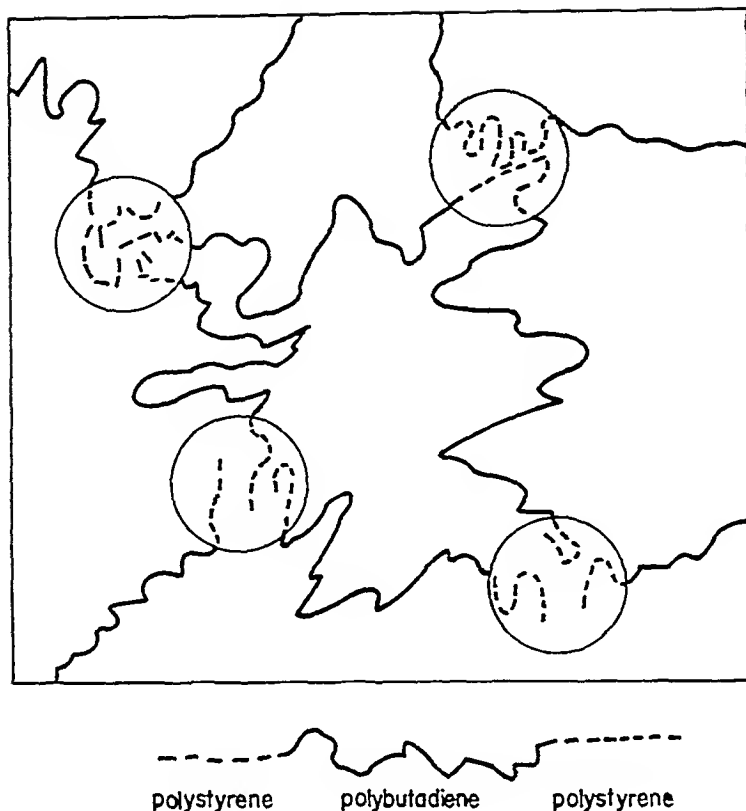


Methyl trichlorosilane is a trifunctional agent.



In either case the coupling is highly efficient, over 90% of the SBLi chains being incorporated into the block copolymer. The examples cited here are useful as elastomers.

At room temperature these thermoplastic elastomers act as though they were covalently cross-linked, exhibiting high resilience and low creep. However, they flow when heated above 100°C like true thermoplastics. The reason is that the large polystyrene blocks form glassy aggregates that function as massive cross-links (Fig. 4-8). The independent behavior of the polybutadiene portion is evident in the behavior of

**FIGURE 4-8**

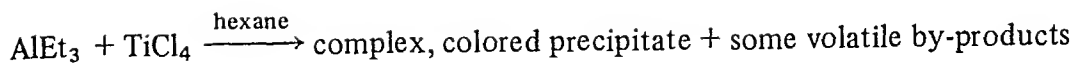
Typical triblock thermoplastic elastomer. Circles are glassy domains of polystyrene acting as temperature-sensitive cross-links holding the polybutadiene segments in place.

dynamic loss with changing temperature (Fig. 4-9). Block copolymers can be made with tensile strengths of over 3000 psi (20 MPa) and high elongations. In contrast, conventional SBR rubber cannot be made to exceed 1 or 2 MPa whether cross-linked or not unless a reinforcing filler is added.

Coordination-Complex Systems

Something of a revolution occurred in the realm of polymer chemistry in 1955 when Giulio Natta demonstrated conclusively that stereospecific polymers could be produced with synthetic catalysts [18]. The systems he employed were primarily α -olefins polymerized by Ziegler catalysts—the discovery of Karl Ziegler. In recognition of this work, Natta and Ziegler shared the Nobel prize in chemistry for 1963. Since the early work, isotactic, syndiotactic, and cis and trans polymers have been made by using ionic and even some free-radical initiators at low temperatures with various types of monomers.

Many systems other than free-radical or ionic have been investigated for the production of polymers. Several have assumed commercial importance because they lead to structures that cannot easily be achieved by free-radical or ionic routes. Ziegler-type catalysts [19] originally involved the formation of a complex precipitate from aluminum triethyl and titanium tetrachloride:



Ethylene bubbled into the suspension at room temperature polymerizes very rapidly to give a high-molecular-weight, linear polyethylene. The linearity leads to higher crystallinity than for branched polymer, so that the product differs significantly from high-pressure, free-radical polyethylene. With propylene, an isotactic polymer can be produced. The mechanism may proceed as outlined in Table 4-5, the stereospecificity stemming from the peculiar topography of the catalyst at the site where monomer is inserted. For a time it was postulated that a heterogeneous catalyst would be needed for stereospecific activity, but this was refuted by subsequent work with similar catalysts, which, though complex, were soluble.

With diolefins such as butadiene and isoprene, both *cis*- and *trans*-1,4 polymers can be obtained. Variations in transition metal halide and/or ratio of alkyl to halide give different structures. For example, $\text{TiCl}_4 - \text{AlR}_3$ with $\text{Al/Ti} > 1$ gives 96% *cis*-polyisoprene and with $\text{Al/Ti} < 1$ gives 95% *trans*-polyisoprene [19].

Metal oxides have been used to give linear polyolefins, although they have not been used for isotactic structures. Nickel, cobalt, chromic, or vanadium oxides supported on silica-alumina have been found effective for ethylene and α -olefin copolymers at low temperatures. In 1975 it could be said that most linear polyethylene being marketed was being produced using the catalyst developed by the Phillips Company (essentially chromium oxide on a silica-alumina base) [20].

4-6 STEPWISE POLYMERIZATION

It is important to realize that in chain reactions, propagation to final molecular weight is very rapid. In the styrene polymerization, for example, we might start a bulk polymerization with a peroxide and stop it after only 1% of the monomer is converted

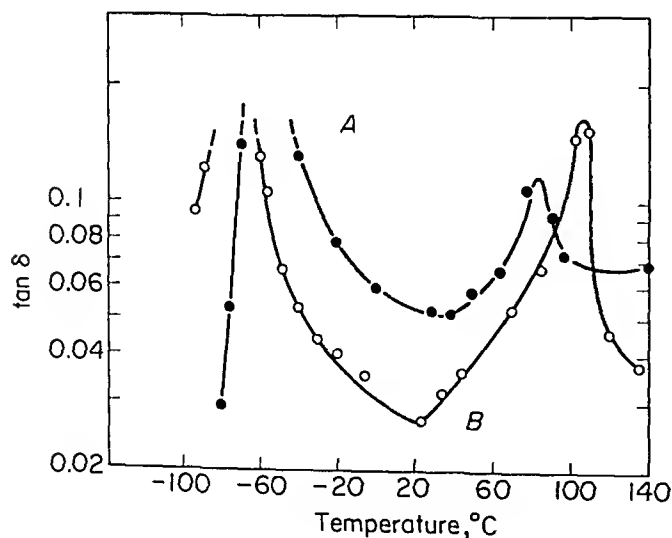
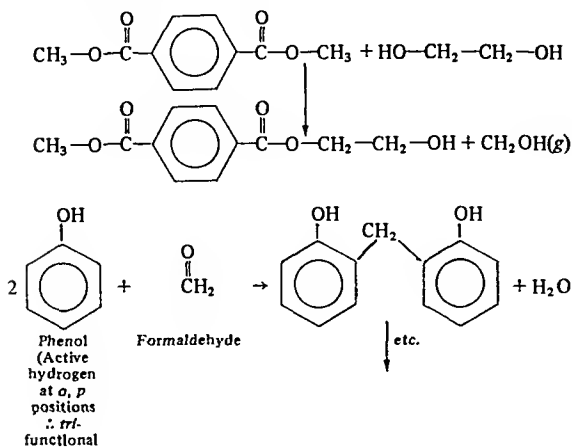


FIGURE 4-9

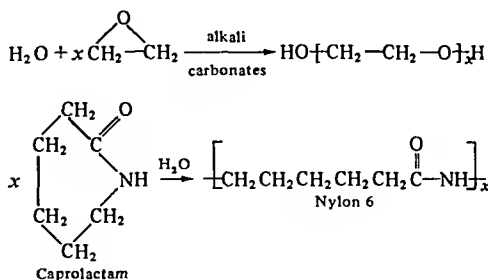
Mechanical loss tangents of styrene-butadiene block copolymers that have been cross-linked. *A* has 6% styrene as blocks and 19% as random units, while *B* has all 25% styrene in blocks of about 350 units. Test run at a frequency of 0.1 Hz [17].

TABLE 4-5
Stepwise Polymerization Systems

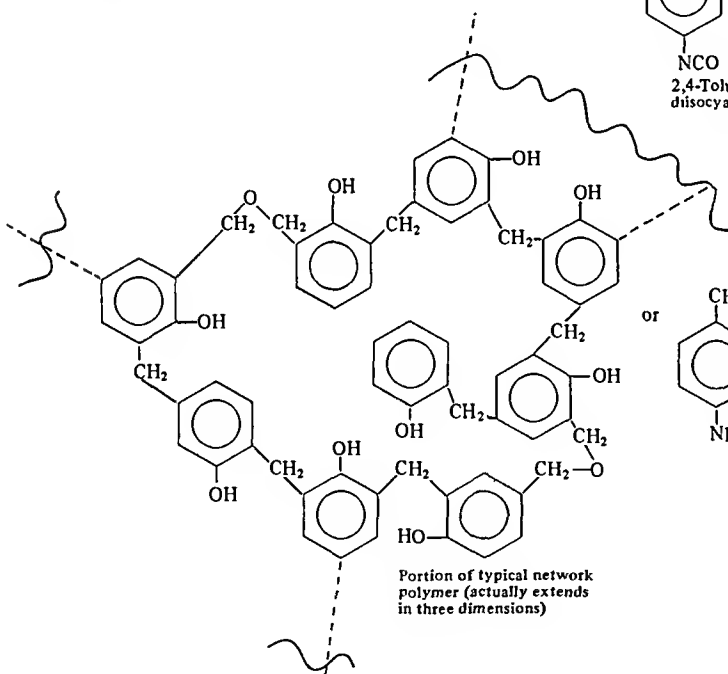
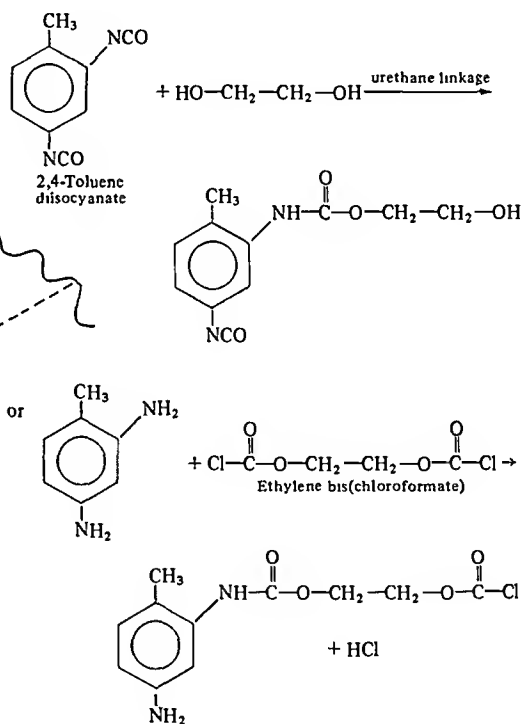
1. Condensation



2. Ring scission



3. Pseudocondensation

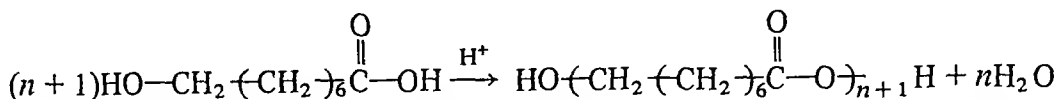


to polymer. Analysis would show that the mixture consisted of 99% unreacted monomer and 1% of a high polymer. Conversion of the rest of the monomer to polymer would not affect the already formed material, which, with the exception of some "living" polymer systems, is dead. We cannot ordinarily make a low-molecular-weight polymer by addition polymerization and then increase its molecular weight by more of the same reaction. This is a major point of difference between chain and stepwise polymerization.

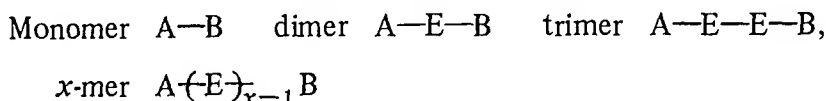
Most reactions other than olefin addition reactions lead to polymer chains containing atoms *other* than aliphatic carbon in the backbone. Another distinction

is that usually polymers formed at early stages of conversion are not dead but can react as easily as monomers. The principle of equal reactivity regardless of molecular weight is fundamental to stepwise polymerization also.

Some reactions involve condensation in that some part of the reacting system is eliminated as a small molecule (Table 4-5). A good example is esterification, where water is eliminated between an acid and an alcohol. Because there is an equilibrium between reactants and products, the rate of conversion can be controlled by the rate of removal of one of the products, namely, water.



If we symbolize reactive hydroxyl by A, carboxyl by B, and the ester group by E, we can write the formulas for monomer, dimer, trimer, etc., as



It is apparent that each successive member of the series has the same reactive groups as the monomer despite its larger size. With the principle of equal reactivity for all molecular sizes, a further condensation reaction is as likely to involve an x -mer as it is monomer. Starting with N_A molecules and forming N_E ester groups, we can define the extent of polymerization p as

$$p = \frac{N_E}{N_A} \quad (4-20)$$

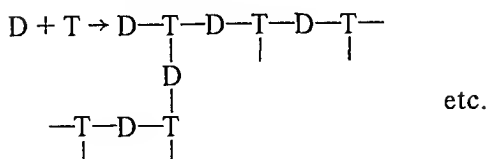
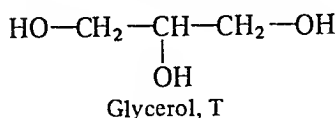
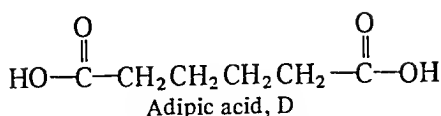
This parameter is zero for pure monomer, and it reaches a value of 1 when every end group has been reacted. The number of molecules left in the system when N_E groups have been formed, N_R , is

$$N_R = N_A - N_E \quad (4-21)$$

The number-average degree of polymerization $\bar{x}_n$ becomes

$$\bar{x}_n = \frac{N_A}{N_R} = \frac{1}{1-p} \quad (4-22)$$

Later (Sec. 6-3) we shall use this example to derive a distribution of molecular weights. Where polyfunctional monomers are involved, successively higher conversion of monomer to polymer increases the probability of forming a network. It is important to be able to predict the maximum degree of conversion to which it is safe to go before network or gel formation occurs. A simple condensation between a trifunctional molecule T, which does not react with itself but does react with a bifunctional molecule D, has been analyzed [21]:



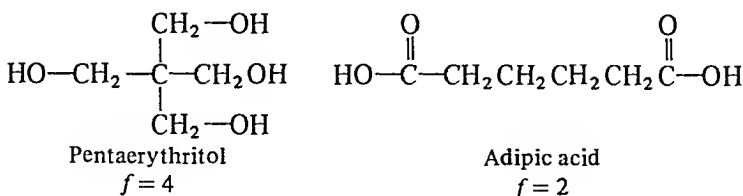
If the initial ratio of hydroxyl groups to carboxyl groups is r and the number of hydroxyl groups and carboxyl groups initially is N_T and N_D , respectively, incipient gelation will take place when $(N_E)_g$ ester groups have been formed, where

$$(N_E)_g = N_T(2r)^{-0.5} \quad (4-23)$$

At this point the probability that each polymer molecule is connected to another one becomes 1; that is, an infinite network has been formed. However, only part of the system is in this network. A substantial amount of polymer remains free and soluble. Further reaction rapidly reduces the soluble, extractable portion. For a monomer of functionality f reacting with another of functionality 2, the fraction of reactive higher-functionality groups that have been consumed at the gel point p_F is given by

$$\left(\frac{1}{p_F}\right)^2 = r(f-1) \quad (4-24)$$

For example, take the case of the esterification of 1.1 mol of pentaerythritol with 2 mol of adipic acid:



The ratio of reactive groups r is $4.4/4.0 = 1.1$. Equation (4-24) indicates that if more than 55% of the hydroxyl groups are reacted ($p_f \geq 0.55$), the system will form a gel. Since r is constant, the fraction of carboxyl groups reacted p_B is simply rp_F , or 0.605. In actual experiments the predictions based on this equation are somewhat conservative because some of the cross-links formed are intramolecular and do not contribute to the total network formation. When there are N kinds of polyfunctional reactants in the same system, an average functionality can be used, where ρ_i is the ratio of reactive groups on reactant i of functionality f_i to all groups that react the same way:

$$\bar{f} = \sum_1^N f_i \rho_i \quad (4-25)$$

In this way $\frac{1}{3}$ mol of sorbitol, $f_i =$ six hydroxyl groups per molecule, with one of ethylene glycol, $f_i =$ two hydroxyl groups per molecule, would be the equivalent of 1 mol of pentaerythritol, both in number of available hydroxyl groups and in average functionality (Table 4-6).

Stepwise reactions can offer special problems in controlling reaction rate and molecular weight. In *ring scission polymerization* there may be a thermodynamic equilibrium that varies with temperature, as in making nylon 6 from caprolactam (see next section).

In many isocyanate systems, reactions can be so rapid as to present special problems in control. Isocyanate foam production involves the following reactions:

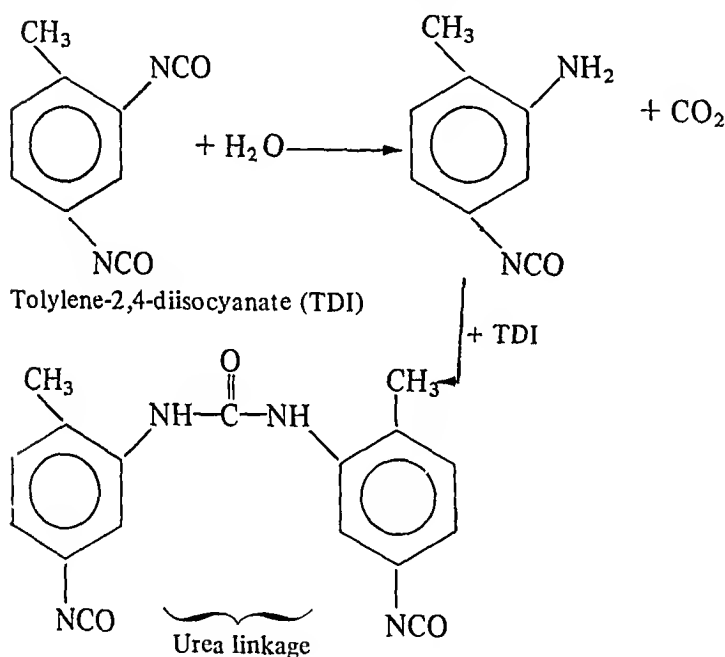
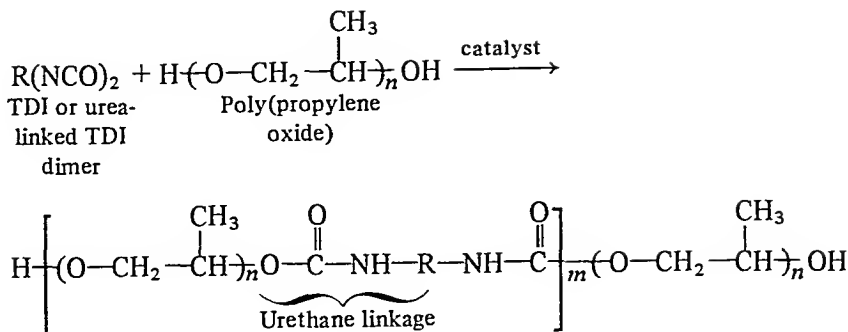


TABLE 4-6
Stepwise Reactions with Polyfunctional Monomers

	Functionality f_i	Initial moles of reactant	Moles of functional group	ρ_i
1. Two reactants, $r = 1.1$				
Pentaerythritol	4	1.1	4.4	1.0
Adipic acid	2	2.0	4.0	1.0
2. Two alcohols, $r = 1.0$				
Sorbitol	6	0.33	2	0.5
Ethylene glycol	2	1	2	0.5
Adipic acid	2	2.0	4.0	1.0

Also:



These reactions are so rapid at room temperature that special machinery had to be developed to bring the ingredients (plus others) together in a matter of seconds, giving a continuous mat of foam product, i.e., the urethane polymer indicated. The important point here is that despite the condensation with ejection of a small molecule, the reaction is not easily controlled.

Stepwise polymerization can sometimes be stopped at an early stage and completed in a separate piece of equipment. Such two-stage polymerizations are quite common. In the isocyanate example above, the poly(propylene oxide) is a low-molecular-weight ($\bar{x}_n = 15$), ring scission polymer which then becomes part of the isocyanate foam by a different reaction. Network polymers often are made in two stages, which may use the same reaction. Phenol-formaldehyde condensation is carried out in two stages (Table 4-5). The first produces a mixture of low-molecular-weight linear and branched polymers that are still fusible and soluble in organic solvents. This reaction may be carried out in a large glass-lined reactor. Final production of the cross-linked network uses the same reaction carried out concurrently with the final forming operation, i.e., molding. This is necessary, because a thermoset material like this cross-linked network cannot be remolded (nor can it be easily removed from a 5000-gal reactor if the first stage proceeds too far too fast).

Many commercially important polyesters and polyamides are made by combining a *dyad* consisting of two dissimilar monomers of functionality 2, A and B, such that A will react only with B and not with itself, and vice versa. The result is something like a copolymer. However, since it is perfectly alternating, it is more convenient to think of it as a dyadic homopolymer. Poly(ethylene terephthalate) and nylon 66, for example, exhibit the regularity and crystallinity typical of homopolymers and are useful as fibers. If one were to use a mixture of diacids rather than a single one in making a polyamide, the result would no longer be a perfect dyadic polymer. The regularity would be disrupted and the tendency to crystallize diminished as in normal random copolymerization.

4-7 RING-SCISSION POLYMERIZATION

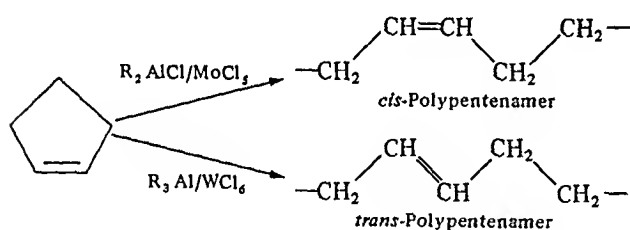
When a ring is opened to form a linear polymer, the propagation step may resemble either chain or stepwise polymerization. It was pointed out in the previous section that an equilibrium may be set up between open-chain and ring structures when the mono-

mer (that is, the ring) is as reactive as growing polymer. In making nylon 6 from caprolactam, no condensation is involved because the product has the same composition as the reactants (Table 4-5). At 220°C with 1 mol of water to 10 mol of monomer initially, an equilibrium is reached rather rapidly in which the reaction mixture contains about 5% unchanged monomer, even though the number-average degree of polymerization is nearly 100 [22]. The residue of monomer can present a problem in purification. It may be necessary to inactivate the equilibration catalyst and then remove the unreacted monomer by vacuum-stripping or by solvent extraction.

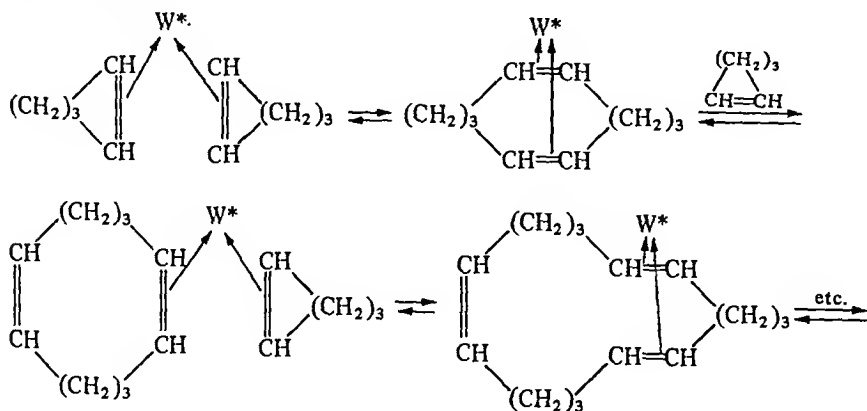
Usually only small rings are involved in such equilibria. The silicones are an exception in that a continuous series of rings of increasing sizes are formed. Silicone rings can be isolated with up to 80 ring atoms (see Sec. 14-7). The polymerization of cyclopentene with a tungsten catalyst also leads to an equilibrium among large rings. A catalyst can be formed from WCl_6 with tetraalkyltin modified by ethyl ether. The combination bears some resemblance to the Ziegler system (Sec. 4-5, Coordination-Complex Systems). The reactions are summarized in Table 4-7. The term *olefin metathesis* has been applied to this reaction [23]. When an acyclic olefin is introduced, the large rings are interrupted and made into open-chain polymers. In one example, monomer is completely converted to polymer in 30 min at 0°C with a ratio of monomer to tungsten of about 10,000. The low temperature is needed to keep the

TABLE 4-7
Ring Scission by Olefin Metathesis [23]

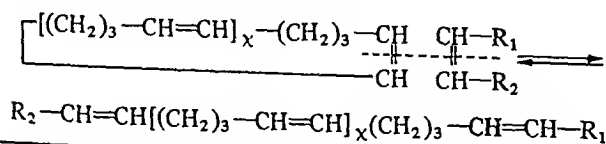
A. Polymerization of cyclopentene



B. Olefin metathesis



C. Cross metathesis with acyclic olefin



equilibrium concentration of cyclopentene down. In general, higher temperatures favor rings over open-chain polymers.

Another common feature of ring-scission schemes is the low heat of polymerization. Polybutadiene has a very similar structure to polypentenamer. But the isothermal conversion of butadiene to polymer requires removal of 17.9 kcal/mol, while conversion of cyclopentene to polymer requires removal of only 4.4 kcal/mol. A commercial polyalkenamer is described later (Sec. 13-4).

4-8 COPOLYMERIZATION

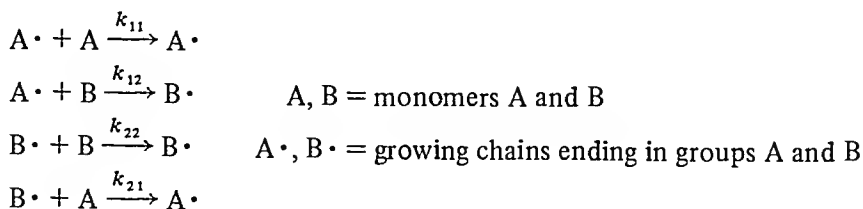
When more than one monomer is polymerized at the same time, a variety of structures can result. In the simple case of two monomers A and B in a chain polymerization, one can derive relationships that will help answer some questions about the degree of heterogeneity of the products made under various conditions:

1. What is the composition of a polymer made from the limited conversion of a mixture of two monomers?
2. How will two monomers that never have copolymerized before interact?

The first is answered by introducing relative reactivities. The second is approached by the Alfrey-Price *Q-e* scheme. To express the relationship of polymer composition to the monomer composition from which it is being formed, we go back to the kinetic scheme of Sec. 4-4. If we can assume that we achieve a "steady-state" population of chain radicals that grow to high molecular weight, the material balances for various species are few and simple for a binary system.

Assumptions

1. Over any short time interval, the concentration of free radicals does not change appreciably with time, that is, $d[\text{radicals}]/dt = 0$.
2. A growing polymer chain's reactivity is determined solely by the last monomer unit added. This reactivity is independent of the molecular weight.
3. The only monomer-consuming reactions taking place, together with their rate constants, are



That is, a growing chain whose last added unit was monomer A has reactivity determined by A only. This chain can add another A, in which case reactivity is unchanged; it may also react with B, in which case the new reactivity is determined by B.

4. Propagation is the only reaction of importance, since it is repeated many times for each initiation or termination step.

Material Balances

1. Rate of creation of radicals ($t = \text{time}$):

$$\frac{d[A\cdot]}{dt} = k_{21} [B\cdot] [A] - k_{12} [A\cdot] [B] = 0 \quad (\text{assumption 1}) \quad (4-26)$$

$$\text{or} \quad \frac{[A\cdot]}{[B\cdot]} = \frac{k_{21} [A]}{k_{12} [B]}$$

2. Rate of consumption (disappearance) of monomers A and B:

$$-\frac{d[A]}{dt} = k_{11} [A\cdot] [A] + k_{21} [B\cdot] [A] \quad (4-27a)$$

$$-\frac{d[B]}{dt} = k_{12} [A\cdot] [B] + k_{22} [B\cdot] [B] \quad (4-27b)$$

We define the relative reactivities as

$$r_1 = \frac{k_{11}}{k_{12}} \quad \text{The ratio of reactivity of monomer 1 (A) toward itself to the reactivity of monomer 1 toward monomer 2 (B).}$$

$$r_2 = \frac{k_{22}}{k_{21}}$$

Now at the instant when monomer concentrations are $[A]$ and $[B]$ (moles per liter), the rate at which monomer is entering a growing polymer chain is $-d[A]/dt$ and $-d[B]/dt$. The mole fraction of monomer A being added to the growing polymer at this instant, F_1 , then is

$$F_1 = \frac{d[A]/dt}{d[A]/dt + d[B]/dt} \quad (4-28)$$

Of course,

$$\frac{F_1}{F_2} = \frac{d[A]}{d[B]} \quad (4-29)$$

Now we let

$$f_1 = \frac{[A]}{[A] + [B]} \quad \text{and} \quad \frac{f_1}{f_2} = \frac{[A]}{[B]} \quad (4-30)$$

Combining Eqs. (4-26) through (4-30) gives

$$\frac{F_1}{F_2} = \frac{(r_1 f_1 / f_2) + 1}{(r_2 f_2 / f_1) + 1} \quad (4-31)$$

$$\text{or } \frac{F_1}{1-F_1} = \frac{r_1 f_1 / (1-f_1) + 1}{r_2 (1-f_1) / f_1 + 1}$$

Thus we have related the "instantaneous" copolymer composition F_1 to the "instantaneous" monomer composition f_1 by two parameters r_1 and r_2 . We say "instantaneous" because if A and B are consumed at different rates so that $F_1 \neq f_1$, the value of f_1 will change as monomer is converted to polymer in a batch operation.

Several cases simplify Eq. (4-31). If k_{12} and k_{21} are nil, no copolymer is formed, only a mixture of homopolymers. If k_{11} and k_{22} are nil, only perfectly alternating copolymer is formed ($F_1 = F_2 = 0.5$). If $r_1 = r_2 = 1$, then $F_1 = f_1$. An interesting special case is $r_1 r_2 = 1$, when Eq. (4-31) becomes

$$\frac{F_1}{1-F_1} = \frac{r_1 f_1}{1-f_1} \quad (4-32)$$

This resembles the vapor y -liquid x composition at constant relative volatility α_r

$$\frac{y}{1-y} = \frac{\alpha_r x}{1-x} \quad (4-33)$$

In such "ideal" copolymerization the F_1 - f_1 curve never crosses the F_1 - f_1 diagonal, whereas when $r_1 r_2 \neq 1$, there can be a point where they cross to give an "azeotrope" at which $F_1 = f_1$ (see Fig. 4-10). Equation (4-31) can be rewritten as

$$Y = r_1 X \frac{1 + r_1 X}{r_1 r_2 + r_1 X} \quad (4-34)$$

where $Y = F_1 / (1 - F_1)$, $X = f_1 / (1 - f_1)$, and r_1 and r_2 are the relative reactivities. Terpolymers (three monomers) require six relative reactivities and can be handled conveniently only in special cases or by computer methods.

For the simple case of only two monomers, the problem of calculating F_1 as a function of degree of conversion and initial monomer composition is analogous to the situation in differential distillation of a binary mixture. Monomer is converted to polymer irreversibly just as volatile liquids are distilled out from a pot irreversibly. A material balance gives the Rayleigh equation [24]:

$$\ln \frac{N}{N_0} = \int_{(f_1)_0}^{f_1} \frac{df_1}{F_1 - f_1} \quad (4-35)$$

where N/N_0 is the mole fraction of all monomer present initially that is still unreacted and $(f_1)_0$ and f_1 are the mole fractions of component A initially and at N/N_0 . This can be integrated graphically or analytically, although the analytic result is not tidy except when $r_1 r_2 = 1$. For that case:

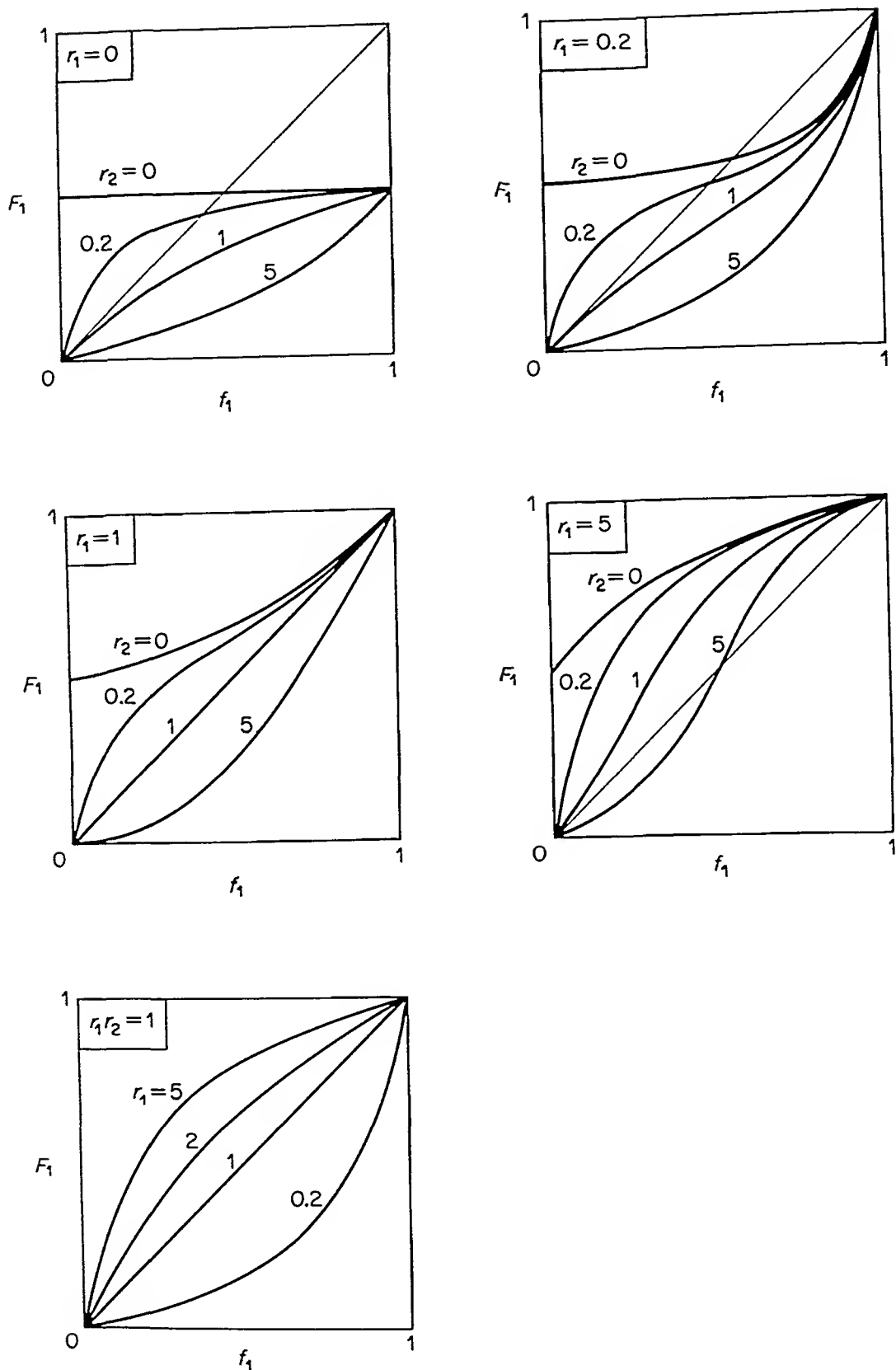


FIGURE 10

F_1 , mole fraction of monomer 1 in polymer formed when f_1 is the mole fraction of monomer 1 in the feed for various combinations of the relative reactivity ratios.

$$\left(\frac{N}{N_0}\right)^{r_1-1} = \frac{f_1}{(f_1)_0} \left[\frac{1-(f_1)_0}{1-f_1} \right]^{r_1} \quad (4-36)$$

Also

$$\frac{N_1}{(N_1)_0} = \left[\frac{N_2}{(N_2)_0} \right]^{r_1} \quad (4-37)$$

where N_1 and N_2 are the number of moles of monomers A and B still in the monomer phase at any time. In the general case [25]:

$$\frac{N}{N_0} = \left[\frac{f_1}{(f_1)_0} \right]^\alpha \left[\frac{f_2}{(f_2)_0} \right]^\beta \left[\frac{(f_1)_0 - \delta}{f_1 - \delta} \right]^\gamma \quad (4-38)$$

where $\alpha = r_2/(1-r_2)$

$\beta = r_1/(1-r_1)$

$\gamma = (1-r_1r_2)/(1-r_1)(1-r_2)$

$\delta = (1-r_2)/(2-r_1-r_2)$

At $(f_1)_0 = \delta$, an azeotrope is formed.

Some results for an equimolar monomer feed of vinyl acetate and vinyl laurate are shown in Fig. 4.11. Although the average polymer composition $\bar{F}_1$ is never changed much and eventually has to equal the original monomer ratio, the polymer

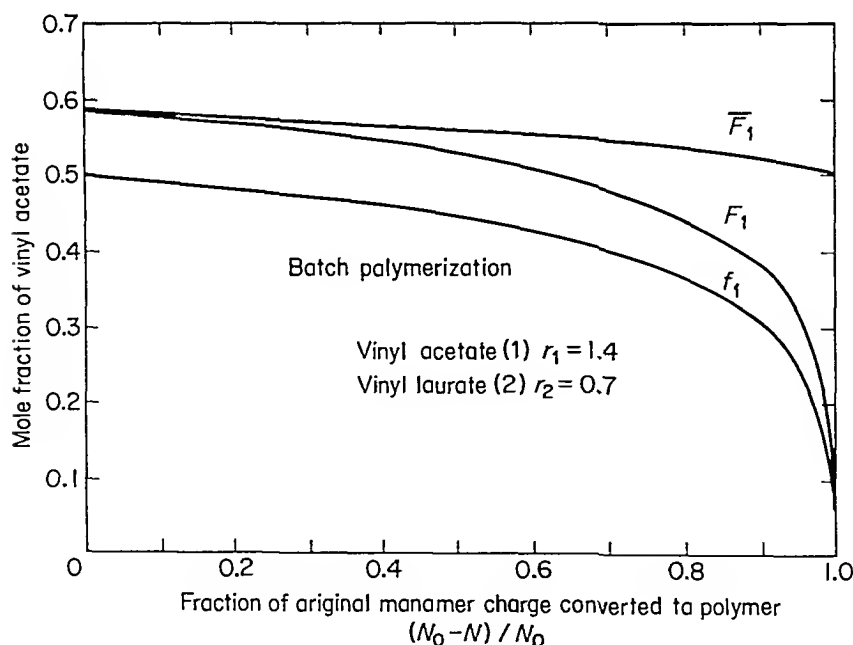


FIGURE 4-11

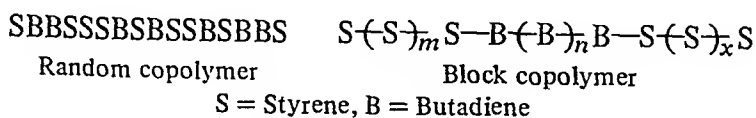
Polymer and monomer compositions as functions of conversion. F_1 is the mole fraction of monomer 1 in the polymer being formed at a point where the feed composition has shifted to f_1 . $\bar{F}_1$ is the average composition of all the polymer generated up to that point.

being made at high conversions may approximate pure vinyl laurate. This is a real problem in polymerization methods that attempt complete conversion. Partial conversion with recycling of unreacted monomer plus makeup of the more reactive monomer is one method of regulation. Another is to add the more reactive monomer during the reaction to maintain the same monomer and therefore the same polymer composition [26]. Some examples (Table 4-8) are typical in that $r_1 r_2$ seldom exceeds unity. A comprehensive set of relative reactivity ratios has been published by Alfrey and Young [27]. However, it is desirable to have some parameters associated with a single monomer that would allow prediction of r_1 and r_2 for various combinations with that monomer just as bond contribution and atomic radii are used to estimate bond strengths and interatomic distances. According to the Alfrey-Price relationship [27, 28], each monomer can be characterized by values of Q and e that are related to relative reactivities by

$$\ln r_1 = \ln \left(\frac{Q_1}{Q_2} \right) - e_1(e_1 - e_2) \quad \text{and} \quad \ln r_1 r_2 = -(e_2 - e_1)^2 \quad (4-39)$$

The parameter Q_1 is mainly affected by the relative stability of the polymer chain radical resulting from the addition of monomer 1 to the growing end. As a point of reference, styrene is assigned values of $Q = 1$ and $e = -0.80$. Resonance-stabilized monomers such as 1,3-butadiene are expected to have high Q values, whereas non-conjugated monomers such as ethylene ($Q = 0.015$, $e = -0.20$) have low Q values. The parameter e is expected to reflect the polarity of the monomer and the polymer radical resulting from the addition of the monomer. An electron-donating substituent on the end of a polymer radical, as in *p*-methoxystyrene ($Q = 1.36$, $e = -1.11$), decreases e , while an electron-withdrawing substituent, as in *p*-nitrostyrene ($Q = 1.63$, $e = 0.39$), increases e . The Q - e scheme is analogous to, but not identical with, the linear free-energy relationship, the Hammett equation, so important to the physical organic chemistry of small molecules. In general the scheme is only moderately successful, but it is useful where experimental data are sparse. Numerous average values have been calculated and tabulated by Young in the previously cited articles.

The copolymers discussed so far are *random* in that we polymerize a mixture of monomers. Even in this case long runs of one monomer or the other may occur, especially when one monomer is present in higher proportion than the other. An extreme case is the *block* copolymer. Sequential addition of butadiene, then styrene, then butadiene to lithium alkyl will give a structure with long runs or blocks of each monomer (see Sec. 4-5, Anionic Systems).



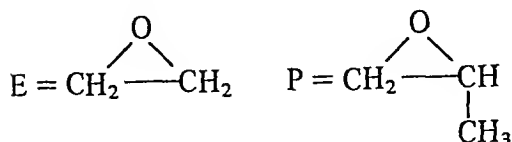
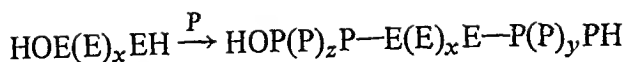
If an ethylene oxide (E) polymer terminating in hydroxyls is used to start a propylene oxide (P) polymerization, a block polymer results with hydrophilic (E) portions and hydrophobic (P) portions. The products at molecular weights of 1000 to 2000 are useful as surface-active agents.

TABLE 4-8
Relative Reactivities and Copolymerization Parameters [27]

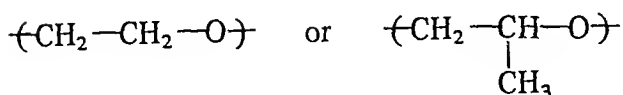
Radical	1,3-Butadiene	Maleic anhydride	Styrene	Vinyl chloride	Methyl methacrylate	Acrylonitrile	Q	e
1,3-Butadiene	1.0	—	1.4	8.8	0.53*	0.35	2.39	-1.05
Maleic anhydride	—	1.0	0.0†	0.008‡	0.03†	0†	0.23	2.25
Styrene	0.5	0.01†	1.0	35	0.50†	0.37	1.00	-0.80
Vinyl chloride	0.035	0.296‡	0.077	1.0	0†	0.074	0.044	0.20
Methyl methacrylate	0.06*	3.5†	0.50†	12.5†	1.0	23†	0.74	0.40
Acrylonitrile	0.0	6†	0.070	3.7	0.0	1.0	0.60	1.20

All data at 50°C except as noted: *5°C, †60°C, ‡75°C.

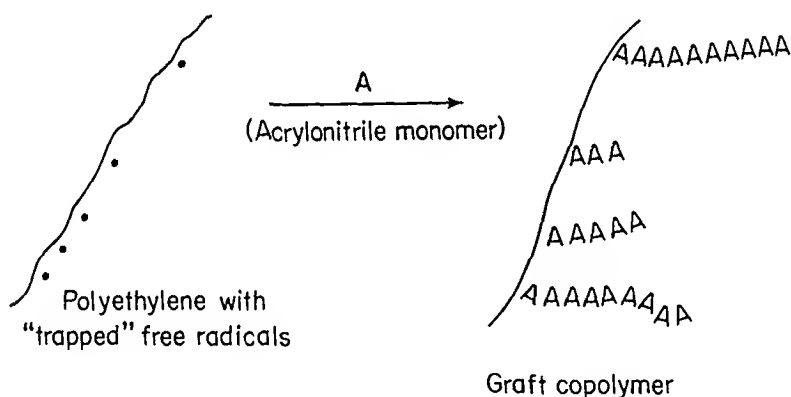
Example: For styrene (1, and acrylonitrile (2), $r_1 = 0.37$ and $r_2 = 0.070$.



or

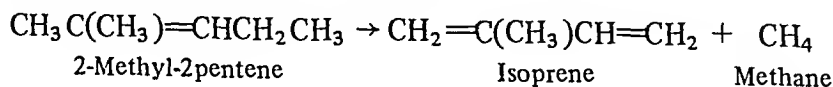
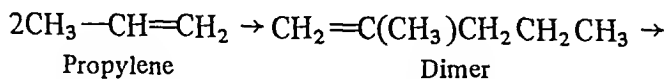


A third variety is the *graft* copolymer. In this case, branches of one monomer are grown on a main stem of a previously formed polymer molecule. For example, polyethylene can be irradiated in air with gamma rays or accelerated electrons, which leave peroxides or free radicals "trapped" on the polymer backbone. Exposed to a reactive monomer such as acrylonitrile ($\text{CH}_2=\text{CHCN}$), polymerization is initiated at the free-radical sites, and branches of poly(acrylonitrile) grow on the polyethylene stem [29].



4-9 BIOSYNTHESIS OF POLYMERS

Polymers produced by biological routes invariably are made by some kind of stepwise polymerization rather than a chain polymerization. An interesting example is afforded by *cis*-1,4-polyisoprene. Isoprene can be made from propylene through a sequence of dimerization, isomerization, and steam demethanization [30]:

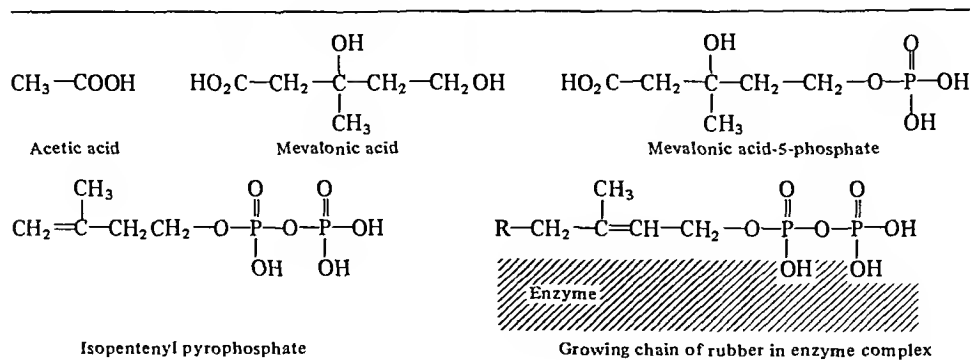


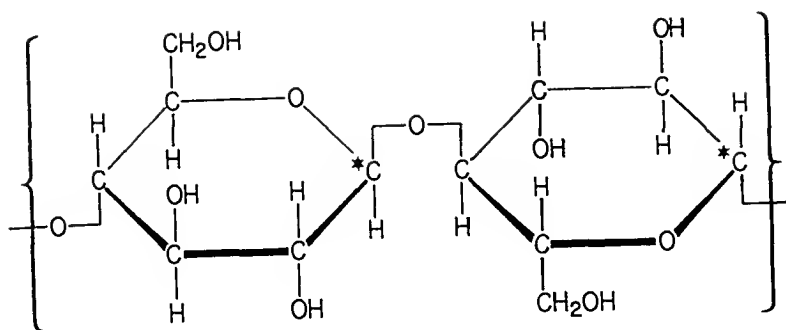
The monomer is easily converted to the *cis*-1,4 polymer by using a butyl lithium initiator in a hydrocarbon solvent (Sec. 4-5, Anionic Systems). The identical structure is produced in the plant tissues of the rubber tree *hevea brasiliensis*. Although over

2000 species of plant produce polyisoprenes, only the one cited is utilized on a large commercial scale, mainly in the warm climates of Malaysia, Indonesia, and Liberia. Brazil, original home of the plant, no longer contributes significantly to the world's supply. Like other plants, the tree contains tubes or vessels that convey water and salts from the roots to the leaves and a second system that carries soluble sugars down from the leaves in the sap. Unlike most other plants, the rubber tree has a third system of vessels in which the sugars are converted into a latex, a stabilized emulsion of rubber particles along with the other compounds necessary to the process such as enzymes, sterols, and lipids. The function of the rubber in the tree is unknown. Apparently it does not serve as a food reserve in the way that starch does in other systems. The primitive raw material used in the latex formation is acetic acid [31, 32]. Many intermediate products have been isolated or have been demonstrated by incorporation of ^{14}C -labeled compounds in the growing plant. A number of enzymes and other catalysts are necessary. Some stages are indicated in the sequence of Table 4-9. The manner in which the pyrophosphate adds to the growing chain and the specific enzyme that is involved are not known with certainty.

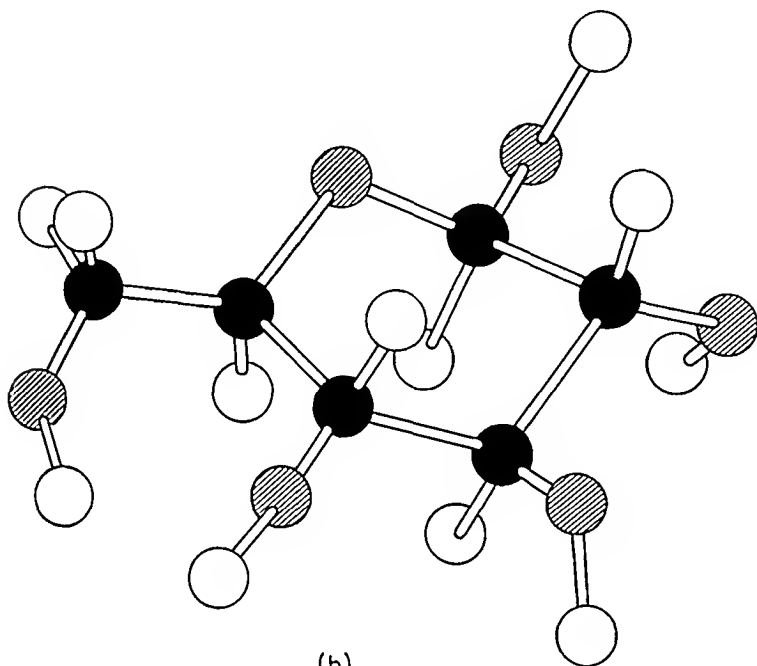
Although most commercially important polysaccharides are recovered from plants and trees, progress has been made in producing some by controlled fermentations in conventional plant equipment. Raw cotton contains over 85% cellulose, which is the linear polymer of β -D-glucopyranose (Fig. 4-12). The formal indication of structure for the pyranose unit is somewhat misleading, since the rings are not planar and the bond angle at the oxygen connecting successive rings is distorted. The important feature to note is that all of the ring carbons are asymmetric and therefore give rise to possible stereoisomers. The changes in physical properties can be great. For example, the unbranched component of starch, amylose, differs only in that the carbon marked with an asterisk in Fig. 4-12 has the oxygen below the ring rather than above as in cellulose. However, amylose dissolves in water but cellulose does not. As in the case of rubber, phosphates appear to be intermediates in the biosynthesis of polysaccharides. Glucose 1-phosphate in the presence of an enzyme extracted from potato juice can be converted to amylose. The energy for carrying out polymerization is obtained by the oxidation of some of the starting monosaccharide. A variety of microorganisms can produce cellulose from sugar in the proper culture medium.

TABLE 4-9
Intermediates in the Biosynthesis of Rubber





(a)



(b)

FIGURE 4-12

(a) Cellulose repeating structure, β -D-glucopyranose unit. (b) D-Glucose.

However, cellulose from such an operation cannot compete economically with polymer from cotton or wood.

At least one polymer has been made commercially by an industrial fermentation [33, 34]. Using corn sugar as a starting material, a polymer of mannose and mannose-6-phosphate is produced that is water-soluble and useful as a thickening agent, emulsifier, or gelling agent in foods, pharmaceuticals, and chemical specialties. In the process the sugar is mixed with yeast extracts and mineral salts and inoculated with a yeast culture. Purification by precipitation, centrifugation, and drying yields 68 lb of polymer from 100 lb of sugar. Further details are given in Sec. 14-3. Sugar itself is a relatively expensive starting material. However, fermentations based on petroleum hydrocarbons show promise of producing intricate polymer structures from inexpensive materials.

The attractive feature of microbial polymerization for industrial purposes is that often a very complex structure of a highly stereospecific nature can be achieved

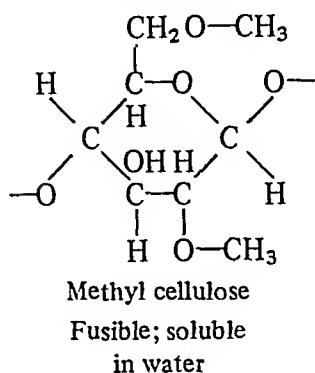
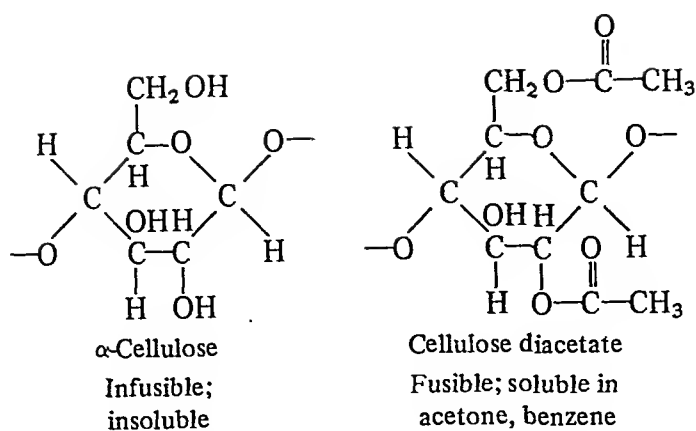
in a single step. The disadvantage is that alterations in structure are difficult to attain. A new strain of yeast or an entirely different bacteria may change some property, but tailoring a molecular weight or a distribution cannot ordinarily be done by a slight change in the catalyst or in growth conditions as is commonly done in nonbiological systems.

The biopolymers discussed here have a relatively simple structure in which a single or a very few repeat units are involved. The enzymes that catalyze these reactions are complex proteins. A large number of laboratories work today on the structure of proteins and other polymeric components of living organisms such as ribonucleic acid (RNA) and deoxyribonucleic acid (DNA). The importance of nucleic acids (combinations of phosphoric acid, sugars, and nitrogenous bases) is that they, in cooperation with proteins, are the main constituents of viruses and genes and occur in all living cells. Synthesis of these materials is remote but conceivable. The production of simpler polymers is much more likely with the present state of the art and certainly less fraught with philosophical, moral, religious, and legal significance than the creation of "test tube life."

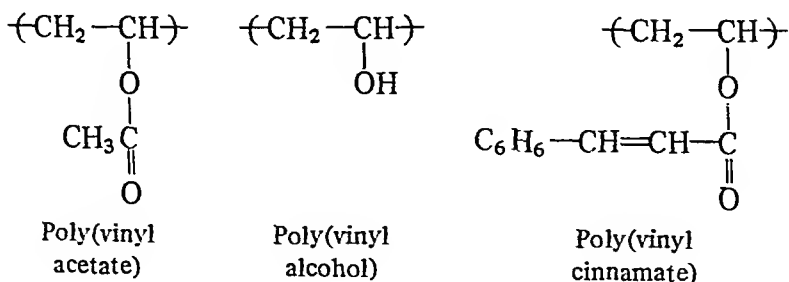
A close approximation to test tube creation of a biologically active substance was made at Stanford University [35]. Using a tritium-labeled (+) DNA as a template, workers were able to make an artificial (−) DNA from modified monomer units. The resulting (−) DNA was different from that usually found in nature, but it was able to act as a reverse template to reproduce (+) DNA identical with the starting material. This experiment does not demonstrate total synthesis of living matter from the elements. It does show that genetic modification by chemical means is a distinct possibility. Total synthesis of an enzyme, the protein ribonuclease A, has been reported (see Sec. 14-4).

4-10 POLYMER MODIFICATION

Whenever a polymer is formed in several stages, each subsequent stage is a kind of polymer modification. All cross-linking reactions (vulcanizations) of rubber would fall in this category together with the molding of network polymers like the phenol-formaldehyde resins. However, the term "polymer modification" is used here to mean changes wrought by the polymer manufacturer in an operation separate from the final molding, spinning, or formation. Modifications are feasible when a polymeric raw material is available that can have its value enhanced substantially by the operation. Two naturally occurring polymers in this category are α -cellulose and natural rubber. In the form of cotton, α -cellulose is already valuable as a fiber. Even with cotton, the chemical treatment to give wash-and-wear properties may amount to a polymer modification. But cotton linters, the short fibers remaining from cotton ginning, and also α -cellulose from wood pulping are not easily utilized. The hydrogen-bonded structure of cellulose prevents it from melting or dissolving below its decomposition temperature. Permanent reaction of these hydroxyl groups by esterification or etherification results in materials that are soluble and fusible—and therefore capable of being molded or cast in useful forms.



Sometimes several purposes can be served at once. Chlorination of natural rubber decreases the flammability of the polymer. At the same time it raises the T_g so that the polymer can be used as a binder for traffic paints. Nitration of cellulose allows the native cotton to be plasticized and molded. Flammability is enhanced at the same time. This may be a disadvantage to makers of molded articles for decoration and apparel. However, the munitions maker regards the flammability and propellant power of guncotton, cellulose nitrate, as its most important advantage. Most often a polymer modification is economically justifiable only when the original polymer occurs naturally or as a by-product. Sometimes modification is the only good way to make a material. A case in point is the photosensitive polymer poly(vinyl cinnamate):



An attempt to polymerize vinyl cinnamate would give a cross-linked network, since the functionality is 4. Even poly(vinyl alcohol) cannot be made directly, because the monomer is unknown (isomeric with acetaldehyde). Thus it is necessary first to

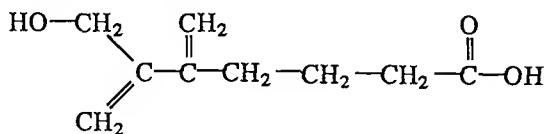
TABLE 4-10
Typical Polymer Modifications

Purpose of modification	Initial polymer	Chemical reactions	Example of final form
Change physical form	α -Cellulose	Regeneration via xanthate	Rayon, cellophane
Change solubility	α -Cellulose	Esterification	Cellulose acetate Cellulose nitrate
		Etherification	Hydroxy ethyl cellulose Carboxy methyl cellulose
			Ethyl cellulose Methyl cellulose
Introduce cross-linking sites	Poly(vinyl acetate)	Hydrolysis	Poly(vinyl alcohol)
	Poly(vinyl alcohol)	Acetal formation	Poly(vinyl butyral) Poly(vinyl formal)
	Butyl rubber	Bromination	Brominated butyl rubber
Increase flammability	Poly(vinyl alcohol)	Esterification	Poly(vinyl cinnamate)
	α -Cellulose	Esterification	Cellulose nitrate (guncotton)
Decrease flammability	Natural rubber	Chlorination	Chlorinated rubber
Change mechanical	Natural rubber	Graft copolymerizations of methyl methacrylate	Graft copolymer

polymerize vinyl acetate, then to hydrolyze the polymer to the polyalcohol. Finally the alcohol is esterified by cinnamic acid (functionality of 1 in an esterification). Exposure of a film of poly(vinyl cinnamate) to ultraviolet light causes rapid formation of a cross-linked, insoluble network (see Sec. 13-5). It is used as a "photoresist" to establish etched patterns on lithographic plates. Some other typical modifications are listed in Table 4-10.

PROBLEMS

- 4-1. What structures can occur in the polymer when chloroprene, $\text{CH}_2=\text{CCl}-\text{CH}=\text{CH}_2$, is polymerized?
- 4-2. Consider the monomer



- (a) What is the functionality of this monomer in a free-radical or ionic polymerization? Name and describe the isomeric forms expected in linear polymers formed by such reactions.

- (b) What is the functionality of this monomer in a polyesterification? Name and describe the isomeric forms expected in linear polymers formed by such a reaction.
- (c) Which would you expect to have the higher T_g , linear polymer from (a) or (b)? Why?
- 4-3. What is the energy of activation for the decomposition of di-*tert*-butyl peroxide (Fig. 4-5)? For bis(1-hydroxy cyclohexyl) peroxide?
- 4-4. Two monomers are polymerized in homogeneous solution with the following results:

Series 1	Monomer A	Monomer B
Initial monomer concentration, mol/liter	0.100	0.200
Time to convert 5% of original monomer charge to polymer, h	0.100	0.300
Initiator concentration, mol/liter	0.0397	0.0397

In a second series at the same temperature, it is desired that both polymers produced initially have the same degree of polymerization. It can be assumed that both polymers terminate exclusively by coupling. In this second series both monomers initially are 0.300 mol/liter. What should be the ratio of concentration of initiator for monomer B compared with that for monomer A in this second series?

- 4-5. The following data are obtained for the polymerization of a new monomer. Predict the time for 50% conversion in run D. Calculate the energy of activation for the polymerization. $R = 1.987 \text{ cal/mol}\cdot\text{K}$.

Run	Temperature, °C	Conversion, %	Time, min	Initial monomer conc., mol/liter	Initial initiator conc., mol/liter
A	60	50	500	1.00	0.0025
B	80	75	700	0.50	0.0010
C	60	40	600	0.80	0.0010
D	60	50	—	0.25	0.0100

- 4-6. This table gives the initial rate of polymerization $(-d[M]/dt)_0$ for each combination of monomer and peroxide in mmol/liter·min. In each case, initial concentrations of monomer and initiator are 0.100 and 0.00100 mol/liter, respectively. Calculate rates (a) and (b).

Monomer	Peroxide I		Peroxide II	
	30°C	80°C	30°C	80°C
A. Styrene	1.00	2.00	0.500	1.50
B. Methyl methacrylate	2.00	5.00	(a)	(c)
C. Vinyl acetate	3.00	(b)	(d)	7.50

- 4-7. Using a k_i based on Fig. 4-5 and $k_p/(k_t)^{0.5}$ from Table 4-2, calculate the time needed to convert half of a charge of methyl methacrylate to polymer using benzoyl peroxide as the initiator in benzene solution at 60°C. What number-average degree of polymerization do you expect initially? Initial charge per 100

ml of solution: 10 g methyl methacrylate and 0.1 g benzoyl peroxide. What fraction of the initiator has been used after 50% conversion of monomer?

- 4-8. When peroxide P is held at 70°C for 10 h, 90% of the original peroxide remains undecomposed. Now if a 5% solution of ethyl mercurate containing 0.000100 mol/liter of peroxide P is polymerized at 70°C, 40% of the original monomer charge is converted to polymer in 1 h. How long will it take to polymerize 90% of the original monomer charge in a solution containing 10% ethyl mercurate (initially) with 0.0100 mol/liter of peroxide P?
- 4-9. Initiator B has twice the half-life that initiator A has at 70°C. Monomer C polymerizes three times as fast as monomer D at 70°C when initiator A is used and all the concentrations are the same. If both C and D terminate by coupling, what is the ratio of degree of polymerization for case I to that of case II?

	Case I	Case II
Monomer	C	D
Initiator	A	B
Concentration of monomer	1 mol/liter	2 mol/liter
Concentration of initiator	0.001 mol/liter	0.005 mol/liter

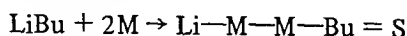
- 4-10. When peroxide A is heated to 60°C in an inert solvent, it decomposes by a first-order process. An initial concentration of 5.0 mmol/liter changes to 4.0 mmol/liter after 1.0 h.
- (a) In the following system what fraction of the monomer should remain *unconverted* after 10 min at 60°C?
- (b) What is the concentration of initiator after 10 min? *System parameters* (all at 60°C):

$$k_p = 1.8 \times 10^4 \text{ liter/mol}\cdot\text{s}$$

$$k_t = 1.45 \times 10^7 \text{ liter/mol}\cdot\text{s}$$

$$\text{Initiator concentration} = 4.0 \times 10^{-4} \text{ mol/liter}$$

- 4-11 Methyl acrylate (1.0 mol) is polymerized in benzene (1.0 liter of solution) using succinic acid peroxide (1.0×10^{-3} mol) at 60°C. How long will it take to convert 10% of the monomer to polymer? How long will it take to convert 90% of the monomer to polymer? If the polymerization were carried out adiabatically, how much would the temperature have risen after 10% conversion? Assume that the specific heat of the benzene solution is 370 cal/°C·liter.
- 4-12. If one reacts butyl lithium (LiBu) with a small amount of monomer, a seed of living polymer is produced.



Now we mix 10^{-3} mol of S with 2 mol of fresh monomer M and find that the reaction is first order in M. Half the monomer, 1 mol, is converted to polymer in 50 min at 25°C. Estimate k_p . Total volume of system is 1 liter. There is no termination reaction.

- 4-13. A vinyl monomer ($\text{CH}_2=\text{CHY}$, mol wt = 213) is polymerized by a free-radical initiator in the presence of dodecyl mercaptan ($\text{C}_{12}\text{H}_{23}\text{SH}$). Analysis of the purified polymer shows:

Number average degree of polymerization = 430

Sulfur content = 5.45×10^{-6} g-atoms/g

Terminal unsaturation = C mol/g

If half the kinetic chains are terminated by coupling and half by disproportionation, what is the expected value of C ?

4-14. Show how the copolymer equation can be rearranged to give:

$$\frac{Y-1}{X} = r_1 - \left(\frac{Y}{X^2}\right) r_2$$

Derive values for r_1 and r_2 from a plot of these data by Dainton [36] for acrylamide (1):methacrylamide (2).

Compositions

Feed $f_1/(1-f_1)$	Polymer $F_1/(1-F_1)$
0.125	0.150
0.250	0.358
0.500	0.602
1.000	1.33
4.000	4.72
8.000	10.63

Plot F_1 versus f_1 and compare the data with the copolymer equation on these coordinates.

4-15. Draw curves (on the same plot) of polymer composition (F_1) versus monomer composition (f_1) for the following systems:

(a) Butadiene (1), styrene (2), 60°C ; $r_1 = 1.39$, $r_2 = 0.78$.

(b) Vinyl acetate (1), styrene (2), 60°C ; $r_1 = 0.01$, $r_2 = 55$.

(c) Maleic anhydride (1), isopropenyl acetate (2), 60°C ; $r_1 = 0.002$, $r_2 = 0.032$.

Assuming that one starts with an equimolar mixture of monomers in each case, which will contain more of monomer (1), the polymer formed first or the polymer formed later?

4-16. Compare the experimental values of r_1 and r_2 from Table 4-8 with those calculated by using Q and e values from the same table for several pairs of monomers.

4-17. Acrylonitrile, 1 mol, is copolymerized with methyl vinyl ketone, 2 mol, at 60°C . Regarding acrylonitrile as monomer 1, $r_1 = 0.60$ and $r_2 = 1.66$. Calculate the mole fraction of acrylonitrile in polymer made initially. What is the mole fraction of acrylonitrile in the polymer being formed when 2 mol of monomer have been converted to polymer?

4-18. In the copolymerization of monomers 1 and 2, $r_1 = 1.0$ and $r_2 = 0.5$. Initially, $f_2 = 2f_1$.

(a) Which monomer predominates in the polymer formed initially?

(b) After 10% of the monomer charge is converted to polymer, does the polymer being made have more or less of monomer 1 than the polymer that was made initially? Show your calculations and reasons.

- 4-19. The molecular weight of polymer when vinyl butyrate is polymerized in an inert solvent is 500,000. With all other conditions the same, addition of 5 g/liter of 1-dodecanethiol decreases the molecular weight to 150,000. What concentration of 1-dodecanethiol will give a molecular weight of 275,000 (other conditions remaining the same)?
- 4-20. Monomers A, B, and C are polymerized together. Illustrate all the possible propagation reactions with equations and constants. Define the relative reaction rates (r_i). What set of values for r_i describes production of mixtures of homopolymers?
- 4-21. Monomer A and monomer B are copolymerized under various conditions. Predict the composition (mol of A) initially formed at the start of a copolymerization with an equimolar feed.

Previous data

Run I: Feed: 99 mol A, 1 mol B. Initial polymer: 0.50 mol B.

Run II: Feed: 1 mol A, 99 mol B. Initial polymer: 2.00 mol A.

- 4-22. Polymer radicals based on methyl acrylate add methyl acrylate monomer at a rate that is only 18% of the rate at which they add styrene. Polymer radicals based on styrene add methyl acrylate at a rate 133% of the rate at which they react with styrene. For what feed composition will a copolymer be produced that is uniform in composition (does not change with conversion)?
- 4-23. The reaction rate of an isocyanate with a primary alcohol may be given by

$$-\frac{d[B]}{dt} = -\frac{d[A]}{dt} = k[A][B]$$

where [B] and [A] are concentrations of isocyanate and hydroxyl groups, respectively, in moles per liter. For the following mixture, estimate the time required for gel to form. Assume $k = 0.50$ liter/mol·h.

3,3'-Dimethylphenylmethanimine-4,4'-	2 mol
diisocyanate($C_{17}H_{14}N_2O_2$)	
2-Ethylhexanol ($C_8H_{18}O$)	1.5 mol
Trimethylol propane ($C_6H_{14}O_3$)	1 mol
Benzene	To make 1 liter

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5

POLYMERIZATION PROCESSES

5-1 DESIGN CRITERIA

Many of the problems that attend mechanical design of polymerization systems are common to ordinary organic reactions. Toxic and flammable monomers and catalysts, noxious odors, and sticky solids are dealt with routinely in chemical and petroleum plants. Some notable examples in the field of commercial polymer processes are:

Toxicity Acrylonitrile ($\text{CH}_2=\text{CH}-\text{CN}$) has the toxicity of inorganic cyanides. A maximal concentration of 20 ppm in air is recommended for 8-h exposures.

Flammability Many Ziegler catalysts involve aluminum triethyl, which is pyrophoric (bursts spontaneously into flames on exposure to air).

Odors The lower acrylates can have odors that are penetrating and disagreeable even in low concentrations. Special catalytic systems may be installed to destroy traces of monomer in effluent gas streams.

In most cases the polymers themselves do not present these problems. On the other hand, unlike low-molecular-weight products, polymers are not generally subjected to purification by extraction, distillation, or crystallization after they have been formed. The ingredients present during formation often remain as part of the final product. Various techniques, bulk, solution, suspension, and emulsion, are used to produce polymers. Some of the criteria for use of these are connected with temperature effects.

The conversion of a double bond to a single bond is accompanied by an exothermic *heat of polymerization* of the order of 10 to 20 kcal/mol. With monomers of molecular weight of about 100 and specific heat of about $0.5 \text{ cal/}^\circ\text{C}\cdot\text{g}$, this means an adiabatic temperature rise of 200 to 400°C . Removal of this heat of polymerization often limits the rate at which the reaction can be carried out, especially because most monomers and polymers are poor conductors of heat. As pointed out earlier, a higher

temperature often gives a lower molecular weight. Because of this, a variable temperature widens the distribution of molecular weights. Also, a rise in temperature increases the rate of reaction and the rate of heat generation. Highly substituted monomers have more steric repulsion in the polymer form. This is reflected in lower heats of polymerization. In Table 5-1, compare styrene with α -methyl styrene and acrylates with methacrylate.

As a monomer is converted to polymer in a homogeneous system, the viscosity can increase rapidly. In a highly viscous medium, small monomer molecules still can diffuse readily to growing chains so that k_p remains relatively constant but large growing chains cannot diffuse easily toward each other, so that k_t can decrease considerably. According to Eq. (4-5), then, the rate should increase. Also, according to Eq. (4-8), the degree of polymerization should increase. This sudden increase in rate, *autoacceleration* or the *Trommsdorff effect*, is pronounced when high-molecular-weight polymer is formed, since the viscosity of the solution increases in proportion to the molecular weight raised to somewhere between the second and tenth power in many cases. The transition from normal kinetics to autoacceleration can be quite sharp. It is aggravated by the higher rate of heat generation, which can raise the temperature and further increase the rate. The addition of large amounts of initiator to give a lower molecular weight or the presence of a solvent to keep the viscosity down can delay the onset of autoacceleration. On the other hand, the addition of a polyfunctional monomer will bring about branching and perhaps gel formation with early onset of the effect.

Polymers invariably are more dense than their monomers even when both are amorphous. The *shrinkage* on polymerization can be as much as 10 to 20%. In a batch polymerization, this often means a variable vapor volume above the reacting liquids. The agitation systems may be complicated, as in the suspension polymerization of styrene or methyl methacrylate, where monomer is lighter than water and must

TABLE 5-1
Heats of Polymerization [1, 2, 3], Liquid Monomer to Amorphous Polymer

Monomer	Structural unit	$-\Delta H_p$, kcal/mol*
1. Ethylene	$-\text{CH}_2\text{CH}_2-$	22.7
2. Propylene	$-\text{CH}_2-\text{CH}(\text{CH}_3)-$	20.5
3. Isobutylene	$-\text{CH}_2-\text{C}(\text{CH}_3)_2-$	12.3
4. Butene-1	$-\text{CH}_2-\text{CH}(\text{C}_2\text{H}_5)-$	20.0
5. Isoprene	$-\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_2-$	17.4
6. Styrene	$-\text{CH}_2-\text{CH}(\text{C}_6\text{H}_5)-$	16.7
7. α -Methyl styrene	$-\text{CH}_2-\text{C}(\text{CH}_3)(\text{C}_6\text{H}_5)-$	8.4
8. Vinyl chloride	$-\text{CH}_2-\text{CHCl}-$	22.9
9. Vinyl acetate	$-\text{CH}_2-\text{CH}(\text{C}_2\text{H}_3\text{O}_2)-$	21.0
10. Acrylonitrile	$-\text{CH}_2-\text{CH}(\text{CN})-$	18.4
11. Methyl methacrylate	$-\text{CH}_2-\text{C}(\text{CH}_3)(\text{C}_2\text{H}_3\text{O}_2)-$	13.5
12. Ethyl acrylate	$-\text{CH}_2-\text{CH}(\text{C}_2\text{H}_5\text{O}_2)-$	18.8
13. Methyl acrylate	$-\text{CH}_2-\text{CH}(\text{C}_2\text{H}_3\text{O}_2)-$	18.8
14. Acrylamide	$-\text{CH}_2-\text{CH}(\text{CONH}_2)-$	19.8
15. Tetrahydrofuran	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{O}-$	5.3

*1 kcal = 4.187 kJ.

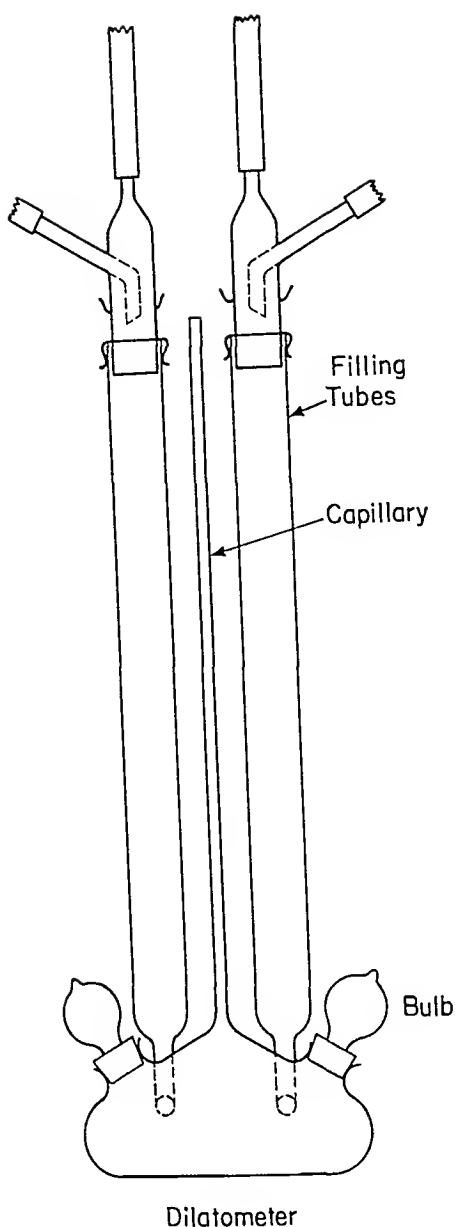


FIGURE 5-1
Dilatometer [4].

be drawn down into the agitated core, but polymer is heavier than water and must be pulled off the bottom of the reactor. This change in volume is the basis for kinetic measurements based on *dilatometry*. Even in dilute (1 to 5%) solutions of monomer in an inert solvent the increase in density is enough to be able to measure continuously the volume of the system and, therefore, the extent of reaction. Usually the density is directly proportional to conversion, simplifying calculations. In the dilatometer shown in Fig. 5-1, the bulb has a volume of about 50 ml and the capillary is 0.1 cm in diameter. Even when a dilute solution of acrylamide, $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}_2$, say 20 g/liter, is polymerized, a 1% conversion of monomer to polymer can be seen as a change in capillary height of about 0.25 cm.

Polymerization may be carried out with monomer alone (*bulk*), in a solvent (*solution*), as an emulsion in water (*emulsion*), or as droplets, each one comprising an individual bulk polymerization, suspended in water (*suspension*). All four methods

are commercially applied to radical-initiated chain polymers such as polystyrene. Most ionic and coordination complex systems are inactivated by water, so that only bulk or solution methods can be used. Also, rather few condensations are carried out in emulsion or suspension. However, ethylene dichloride and sodium polysulfide are condensed to give ethylene polysulfide rubber and sodium chloride in an aqueous emulsion. Gas-phase polymerization and interfacial condensation are special techniques, which are mentioned under solution polymerization.

5-2 BULK POLYMERIZATION

In bulk polymerization, also called *mass* or *block* polymerization, monomer and polymer (and initiator) are the only components. When only part of the monomer charge is converted to polymer, however, the problems encountered are more typical of the solution method, which is discussed next. We can differentiate between quiescent and stirred bulk polymerizations. Both methods are applied to systems where polymer is soluble in monomer and progressively increases in viscosity with conversion. In quiescent systems, gel formation, corresponding to infinite viscosity, can occur. Because of the heat of polymerization and autoacceleration, reaction rate is difficult to control. Heat removal is impeded by high viscosity and low thermal conductivity. The removal of traces of unreacted monomer from the final product is difficult because of low diffusion rates. Conversion of all monomer is difficult for the same reason.

Quiescent Bulk Polymerization (Monomer Casting)

Typically, nonstirred polymerizations are used to produce materials in useful shapes. Phenol-formaldehyde condensation carried out in a mold under pressure is an example that has been mentioned before. The casting of poly(methyl methacrylate) sheet has several advantages. For example, the Trommsdorff effect gives a large fraction of extremely high molecular weight molecules. These in turn make for a tough material with high melt viscosity that is ideal for sheet-forming operations. It would be hard to make this material in another form and then mold it as sheet because of this high melt viscosity. The major problems involved are (1) heat removal to prevent boiling of monomer, which would leave bubbles in the sheet; (2) conversion of all monomer; and (3) accommodation of the 21% shrinkage that occurs on polymerization. Problems 1 and 3 are alleviated somewhat by filling the mold with a degassed syrup of low-molecular-weight polymer (10 to 30% of syrup) and benzoyl peroxide (0.02 to 0.05%) in methyl methacrylate rather than with monomer alone. The mold consists of two glass plates separated by a flexible gasket that is also the confining wall of the mold (Fig. 5-2). After filling, the entire assembly is placed in an air oven. A typical time-temperature profile (Fig. 5-3) shows an exotherm due to autoacceleration after about 18 h. The shrinkage is accommodated by the flexible mold wall. Virtually complete conversion of monomer is assured by a 10-h "soak" at 85°C.

Stirred Bulk Polymerization

Although polystyrene and poly(methyl methacrylate) are commercially produced in stirred continuous-bulk systems, mechanical details of the processes are not readily

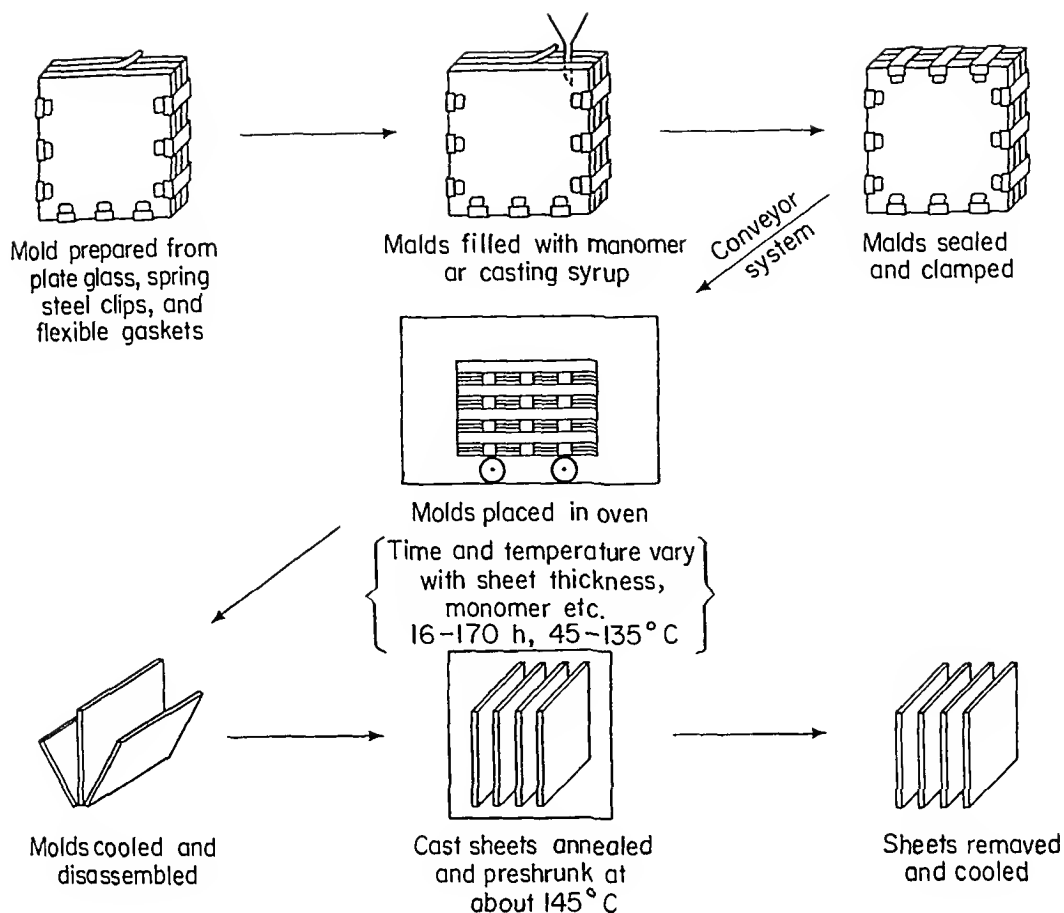


FIGURE 5-2
Casting methyl methacrylate sheet [5].

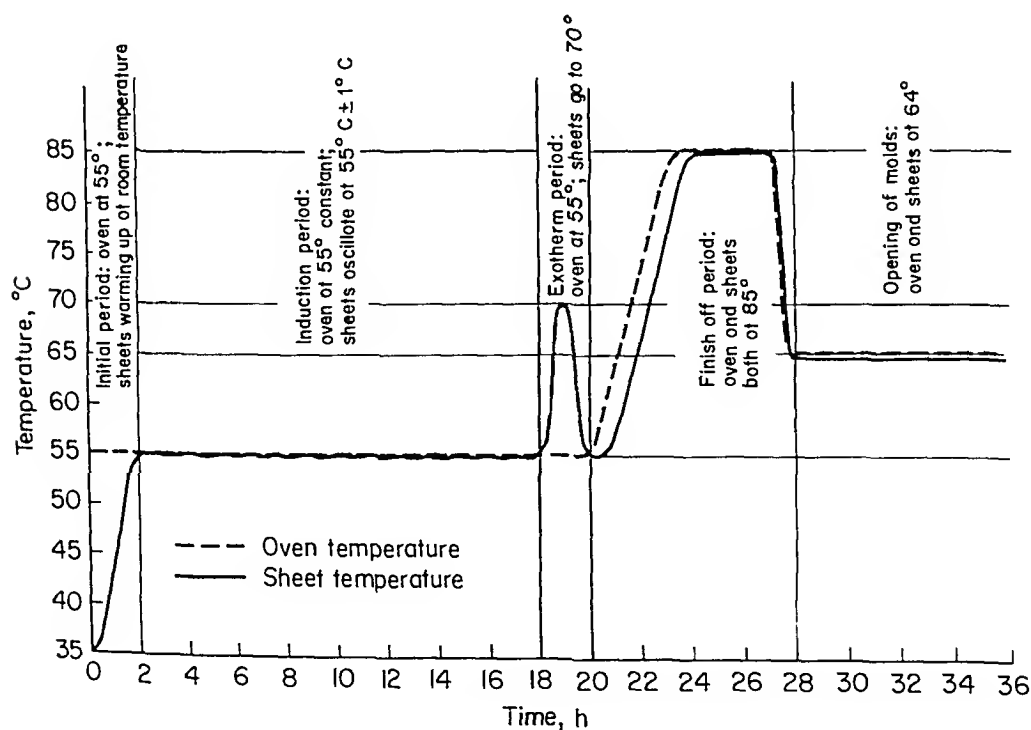
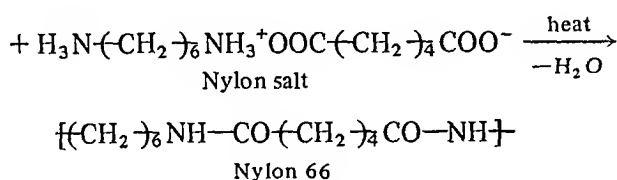


FIGURE 5-3
Typical curing cycle for 0.25-in-thick, clear, cast sheet from methyl methacrylate syrup [6].

available. In some cases, conversion is limited to less than 70% or so, and the remaining monomer is stripped and recycled. These are, in effect, solution polymerizations and are treated in the next section. Equipment that will handle liquids progressively from monomer (*ca.* 0.01 poise) to polymer (*ca.* 10^5 poises) with efficient heat removal is usually specifically designed for a given installation. Conventional turbine- or propeller-agitated vessels can handle a limited degree of conversion. With low-molecular-weight condensation polymers, the completed polymer melt may be transferable by gear pumps or merely extruded from the reactor by application of moderate pressure. Nylon 66 is sufficiently low in viscosity above its melting temperature that it can be pumped through spinnerets (small orifices) directly from the polymerization vessel. In one design (Fig. 14-9) the continuous reactor consists of a series of tubes where nylon salt is first heated, water is flashed off, and finally the molten polymer is extruded directly from



the reactor. High-molecular-weight materials need special equipment similar to screw extruders to convey the melt and remove heat simultaneously (Fig. 5-4). Usually in these continuous systems, high temperatures employed in the later stages are used in order to assure flow of the melt and complete reaction of monomer. This works in the opposite direction from the Trommsdorff effect as far as molecular weight is concerned, so that a lower average molecular weight is obtained than by quiescent polymerization.

5-3 SOLUTION POLYMERIZATION

The main advantage of a diluent is to take up heat of polymerization by a rise in temperature or by vaporization. We can subdivide solution polymerizations by the phases present. Invariably, monomer and diluent are miscible, so the combinations are:

	1	2	3	4
Monomer and diluent	Soluble	Soluble	Soluble	Soluble
Initiator	Soluble	Insoluble	Insoluble	Soluble
Polymer	Soluble	Soluble	Insoluble	Insoluble

Some physical schemes to carry out these reactions can be illustrated with specific examples.

1. *All components soluble.* In one process [8], ethylene containing a trace of oxygen (initiator) is compressed to 2000 atm and continuously pumped to a heated tube 5 mm ID and 20 m long (Fig. 5-5). With an average residence time of 45 s at 175°C, 22% of the ethylene is converted (3 kg polymer/h). At the end of the tube

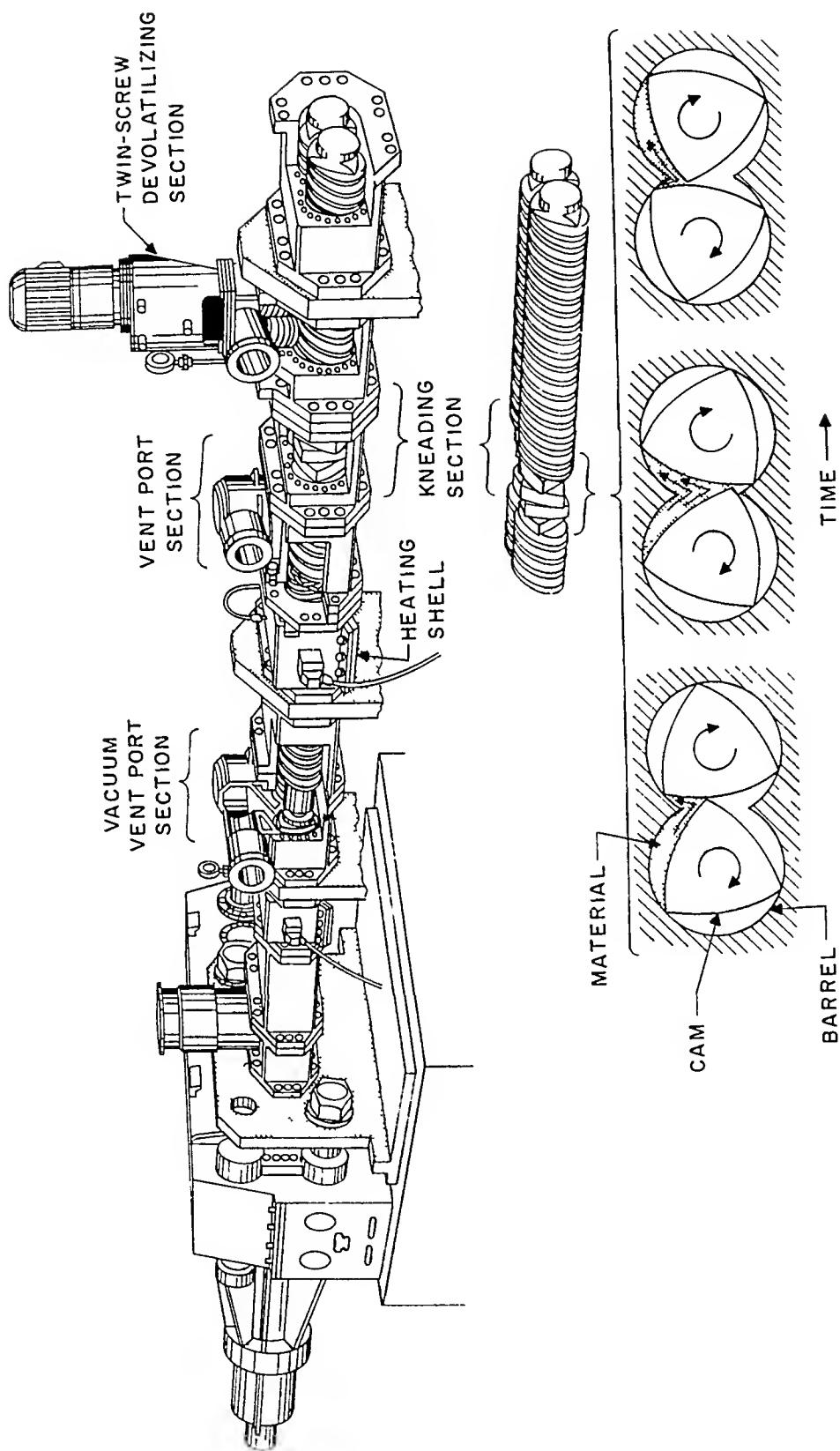


FIGURE 5-4
Twin-screw extruder reactor (courtesy of Werner and Pfleiderer Corp.) [7].

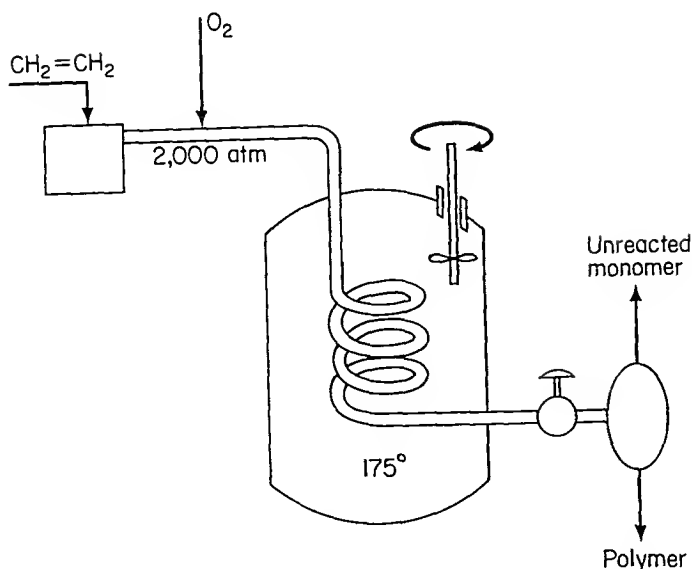


FIGURE 5-5
Tubular reactor for ethylene polymerization.

a valve is opened at intervals and the pressure drops slightly as polymer and monomer are ejected in a cyclic manner. The monomer flashes off, leaving polymer to be washed, dried, and packed. In this pilot-scale example, the monomer is the diluent. The extreme pressure favors the tube geometry. In a production unit the tube can be over a kilometer in length. Stirred autoclaves operating at 2000 to 3000 atm are sometimes used in place of the tubular geometry. Further details are given in Sec. 13-2.

2. *Insoluble initiator.* A chromia silica alumina catalyst (an initiator that can be regenerated) will convert ethylene to linear polymer at moderate pressures. One method [8] is to pass a dilute (2 to 4%) solution of ethylene in a saturated hydrocarbon over a fixed bed of catalyst at 150 to 180°C and 300 to 700 psi (2.1 to 4.8 MPa) (Fig. 5-6). Conversion may be high, but there is a considerable volume of solvent to recover and recycle. Periodic reactivation of catalyst at about 50-h intervals is required.

3. *Insoluble initiator and polymer.* With a polymerizing system of ethylene and an agitated catalyst suspension at lower temperatures, polyethylene and catalyst may be insoluble and form a slurry which is removed continuously (Fig. 5-7). If productivity (ratio of polymer formed to catalyst charged) is high enough, simple drying may suffice. If not, washing out of catalyst may be needed.

A fluidized-bed, gas-phase polymerization bears some resemblance to the process just described. Fine catalyst particles are contacted with rapidly upward-moving ethylene vapors below the melting point of polyethylene. This has become an important commercial process with definite economic advantages over solvent-based systems (see Sec. 13-2).

4. *Insoluble polymer.* Heating an aqueous solution of acrylonitrile with persulfate as initiator at 80°C results in a stringy precipitate of polyacrylonitrile that can be filtered out and dried.

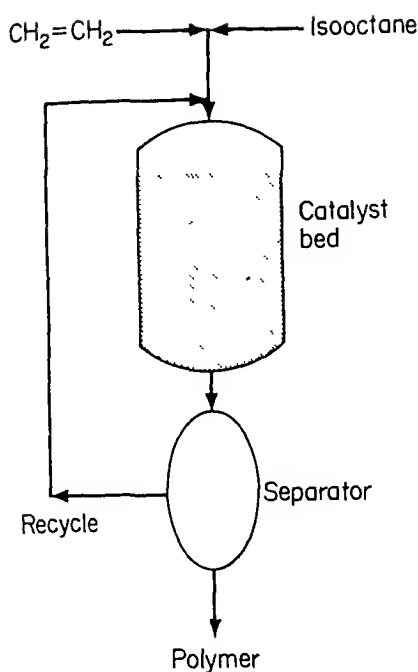


FIGURE 5-6
Fixed-bed reactor.

An interesting example of condensation polymerization in this category is *interfacial condensation* [9]. A diacid chloride is dissolved in a heavy, dense solvent such as tetrachloroethylene. As a stagnant layer above it is poured a solution of diamine in water. At the interface a layer of polyamide (nylon) is formed almost immediately. But the reaction stops because of the slow diffusion of reactants to each other through the polymeric interface. However, as the interface is pulled out, reactants contact each other and form more polymer (Fig. 5-8). Within limits, the rate of reaction is controlled by the rate of interface removal. With pure sebacoyl chloride and

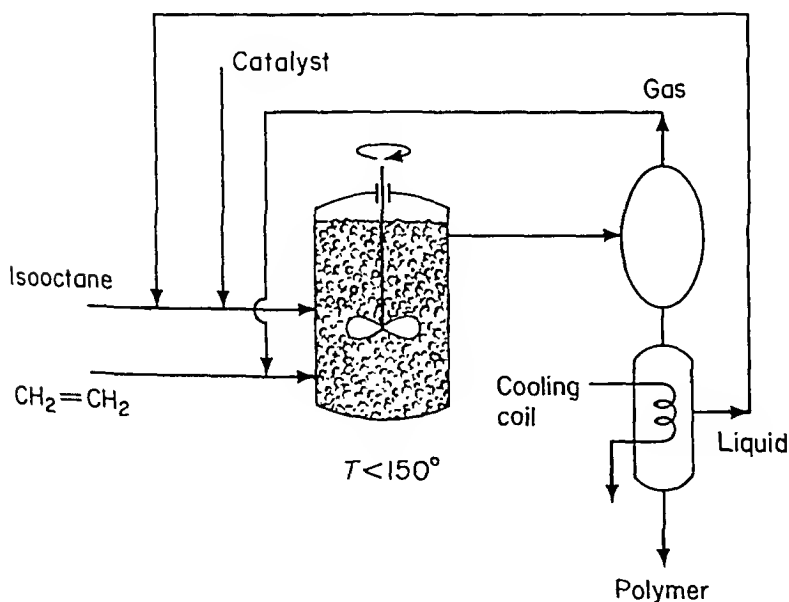


FIGURE 5-7
Slurry reactor.

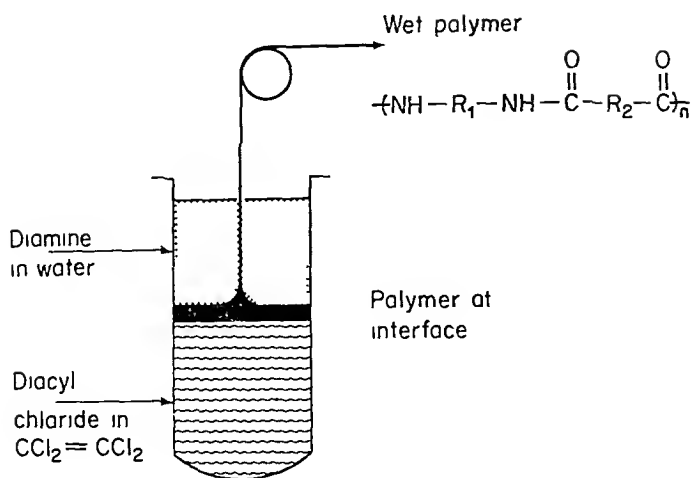
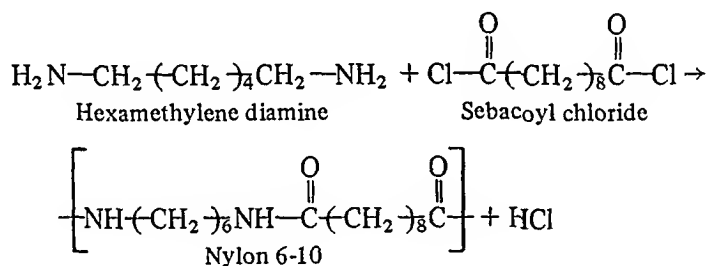


FIGURE 5-8
Interfacial condensation.

hexamethylene diamine, nylon 6-10 is formed from which fibers or films can be made.



The demonstration based on the apparatus of Fig. 5-8 has been popularized under the name "The Nylon Rope Trick" [9-11]. It has been used at countless science fairs and at all levels of sophistication from elementary school to university. On the other hand, it is not very convenient even for laboratory preparations. A typical preparative method starts with the same ingredients as the nylon rope trick. The aqueous phase is placed in a high-speed stirrer (blender) and the organic phase added while the system is stirred at high speed. Suspending agents or surfactants may be added to stabilize the polymer-solvent dispersion which results. Plant-scale operations also use stirred tanks rather than quiescent interfaces.

For all these systems a conventional glass-lined or stainless-steel reactor is suitable for batch operations when reaction pressures and product flow characteristics are within certain limits. Recently, scraped-surface, stainless-steel reactors have been built that will handle pressures from a full vacuum to 6 atm and viscosities of 1 mPa·s to 10 kPa·s for large batches.

5-4 SUSPENSION POLYMERIZATION

If the monomer is insoluble in water, bulk polymerization can be carried out in suspended droplets. The water phase becomes the heat transfer medium. Since it is the

continuous phase, viscosity changes very little with conversion, so that heat transfer to the reactor walls can be efficient. The behavior inside the droplets is very much like the bulk polymerizations previously described. But because the droplets are only 10 to 1000 μm in diameter, more rapid reaction rates can be tolerated without boiling the monomer. To keep the droplets from coalescing as they proceed from liquid to solid states via a sticky phase, a protective colloid (suspending agent) and careful stirring are used. Poly(vinyl alcohol) dissolved in the aqueous phase is a typical suspending agent. Electrostatic charges are induced on the suspended monomer-polymer particles, which retard coalescence. They do not prevent the particles from rising (creaming) together if agitation is stopped. The particle size and size distribution are affected by the suspending agent and stirring rate. In the particle diameter range of 10 to 1000 μm , Fondy and Bates found that particle diameter varied inversely with impeller tip speed raised to the 1.8 power for a variety of impeller designs [12].

A simple example of suspension polymerization can be carried out in a glass flask with agitation.

Aqueous phase:

Water	400 ml
Poly(vinyl alcohol)	1 g

Oil phase:

Methyl methacrylate	100 g
Benzoyl peroxide	1 g

Under a nitrogen atmosphere the aqueous phase is heated to 80°C. The oil phase is added with stirring at about 150 to 300 rpm with a paddle agitator. After an hour or so a slight exotherm, 5 to 10°C, is noted. Particles of the slurry examined before this time are sticky and usually agglomerate on cessation of stirring. After the exotherm, when most conversion has taken place, the particles are hard and do not agglomerate. Initially the monomer phase is lighter than water and agitation near the surface is essential. After the exotherm, enough polymer has been formed to make the oil phase heavier than water, so that settling out occurs if stirring is inadequate. Final recovery of the beads, which are 100 to 1000 μm in diameter, is by filtration and washing.

In most cases, polymerization is carried to high conversion and pearl-like beads of polymer result, especially if the polymer is amorphous and below its glass-transition temperature. Two important exceptions are vinyl acetate and vinyl chloride. Vinyl acetate can be polymerized to give a stable suspension of about 50% solids content if the particle size is kept small (1 to 15 μm diameter). Plasticized with castor oil so that the polymer will be above T_g at room temperature, the suspension makes an excellent quick-setting adhesive for wood, paper, and cloth. Poly(vinyl chloride) is insoluble in its monomer. Suspension polymerization can be carried to 70 to 90% conversion under moderate pressure (6 atm) and temperature (80°C) by using an oil-soluble initiator such as lauroyl peroxide or azoisobutyronitrile. During this period, polymer precipitates in the droplets. Release of pressure and stripping of monomer by pulling a vacuum leaves the polymer portion of the droplets as porous particles that can be recovered by filtration and drying or directly by spray drying. Such porous particles are ideally suited for adsorbing plasticizers in "dry-blending" operations.

A combination of solution suspension and network polymerization has been used for a special-purpose material. Moore [13] describes the copolymerization of styrene with divinyl benzene as a 20% solution in toluene with peroxide initiator. All these ingredients are suspended in water. The swollen-gel droplets that result are well suited for gel permeation chromatography columns (Sec. 6-4). Ion-exchange resins can be made from cross-linked suspension-polymerized droplets (without the solvent), since the physical form does not have to be changed and the subsequent reactions can be performed on the beads. Sulfonation of styrene-divinyl benzene copolymer beads leads to a strong-acid ion exchanger (see Sec. 13-3 and Fig. 13-10).

5-5 EMULSION POLYMERIZATION [14]

Some important distinctions between emulsion and suspension polymerizations are:

1. Emulsions usually are comprised of small particles, 0.05 to 5 μm , compared with suspensions, particles 10 to 1000 μm diameter.
2. Water-soluble initiators are used rather than monomer-soluble.
3. The end product usually is a stable *latex*—an emulsion of polymer in water rather than a filterable suspension.

Because of these conditions, the mechanism of polymerization is basically different. The essentials of an emulsion polymerization system are monomer, a surface-active agent (surfactant), initiator, and water. Initially, the surfactant is in the form of micelles, spherical or rodlike aggregates of 50 to 100 surfactant molecules with their hydrophobic “tails” oriented inward and their hydrophilic “heads” outward. These micelles form whenever the concentration of surfactant exceeds a rather low “critical micelle concentration.” The manner in which the critical micelle concentration for a given surfactant is measured is instructive for our purposes. If a dilute aqueous solution of an oil-soluble dye like eosin is titrated with a dilute soap solution, a soap concentration is reached where the color suddenly disappears. The explanation is that the dye has dissolved in or has been extracted by the micellar interiors. This is the same point at which surface tension stops decreasing rapidly with added soap. If monomer is added to a micellar dispersion, most of it remains as rather large droplets, but some of it dissolves in the micelles just as the dye does. Since they are smaller, the micelles present much greater surface area than do the droplets. Consequently, when free radicals are generated in the aqueous phase, the micelles capture most of them.

After a few percent conversion, the system consists of (1) stabilized, monomer-swollen polymer particles rather than micelles and (2) monomer, which is still mainly in droplets, although it constantly diffuses to replenish the swollen particles where polymerization continues. The result is, when monomer is quite water-insoluble,

$$R_p = k_p [M] [M \cdot] \quad (5-1)$$

where $[M]$ now is the concentration of monomer in the swollen polymer particles. Since this concentration, moles per liter of swollen particles, may remain constant from low conversions up to 70 or 80% conversion, R_p should be independent of the

total concentration of monomer, i.e., moles per liter of emulsion. This means that the superficial reaction rate is pseudo-zero order in monomer. Now, it can be shown that a polymer particle cannot tolerate more than one growing chain at a time. Two radicals in the same particle mutually terminate rapidly. Therefore, on the average half the particles will contain radicals at any instant. As an analogy, picture a group of cups standing in the rain. Each cup has received either an odd or an even number of raindrops. With enough cups and enough rain, the chances are that half the cups have received an even number of drops and the other half an odd number. If the raindrops are initiating radicals and the cups are polymer droplets, only the half that have received an odd number of droplets are growing, the even cases having been stopped by mutual termination.

So $[M\cdot]$ is simply $N_p/2$, where N_p is the number of particles per unit volume of emulsion and

$$R_p = \frac{k_p [M] N_p}{2} \quad (5-2)$$

Similar reasoning, disregarding chain transfer, and assuming termination by coupling, gives

$$\bar{x}_n = \frac{k_p N_p [M]}{d[M\cdot]/dt} \quad (5-3)$$

where $d[M\cdot]/dt$ is the rate of radical formation (not the *net* rate) and may be proportional to the square root of initiator concentration in the aqueous phase.

The number of particles per unit volume, N_p , can be related to the concentrations of surfactant and initiator. The derivation can be complex, but the Smith-Ewart approach [14, 15] introduces a number of simplifying assumptions. The entire process of establishing N_p takes place during the first part of polymerization when the surfactant is still present in the form of micelles. Each effective radical generated from the initiator converts a micelle into a swollen polymer particle, which then grows at a constant rate ($\mu = dv/dt$). The capture of radicals by particles in competition with micelles is ignored for the moment. Every particle formed grows in area as well as in volume. Each increment of area requires a coating of surfactant, which is obtained from unreacted micelles. Thus micelles disappear for two reasons: Some are converted to polymer particles, and some supply surfactant to growing particles.

At some time t_1 all the surfactant in the system has coated the surface of particles, leaving none in the form of micelles. At that point, N_p no longer changes and the rate of polymerization is given by Eq. (5-2). If effective radicals are being generated constantly at a rate ρ_r and each one starts a particle, then at t_1

$$N_p = \rho_r t_1 \quad (5-4)$$

Next, we can relate t_1 to the surface area of particles being formed.

1. A single particle is formed at time τ and then grows until time t_1 . The volume of this particle (neglecting the initial volume of the micelle) at this time will be

$$v(t_1, \tau) = \mu(t_1 - \tau) \quad (5-5)$$

The surface area of the particle is related to the volume by geometry:

$$a(t_1, \tau) = (36\pi)^{1/3} [\mu(t_1 - \tau)]^{2/3} \quad (5-6)$$

2. The number of particles generated in the time interval $d\tau$ is $\rho_r d\tau$. Thus the total surface area of particles at t_1 , using Eq. (5-6), is:

$$A_t = \int_0^{t_1} a(t_1, \tau) \rho_r d\tau = (36\pi)^{1/3} (0.6\rho_r) \mu^{2/3} t_1^{5/3} \quad (5-7)$$

3. The total area at t_1 is also given by

$$A_t = a_s [S] \quad (5-8)$$

where a_s is the surface area occupied by a mole of surfactant and $[S]$ is the surfactant concentration in mol/liter.

4. Combining Eqs. (5-4), (5-7), and (5-8), we can eliminate A_t and t_1 :

$$N_p = 0.53 \left(\frac{\rho_r}{\mu} \right)^{0.4} (a_s [S])^{0.6} \quad (5-9)$$

The total number of particles per liter should vary with surfactant concentration to the 0.6 power and with initiator concentration (via ρ_r) to the 0.4 power. As noted earlier, at time t_1 (usually corresponding to a very small fraction of conversion) N_p no longer increases and the rate of polymerization reverts to Eq. (5-2). This derivation can be modified to take into account radicals entering particles in competition with micelles. The only change is that the factor 0.53 becomes 0.37. More serious differences occur when particles are large, when initiator decomposition is very slow, or when the monomer is partly soluble in water or insoluble in polymer [15]. However, the form of Eq. (5-9) often holds even though the proportionality factor must be determined experimentally.

An increase in surfactant concentration increases N and, therefore, increases R_p and $\bar{x}_n$ (Fig. 5-9). High molecular weights are possible in emulsion polymerization because initiation is in one phase, water, and termination is in another phase, monomer-polymer. The combination of high molecular weight with high rate is one reason for the popularity of this method. *Seeded polymerizations* can be useful for making large-particle-size latexes. A completed "seed" latex is diluted to give the desirable value of N_p particles per liter of emulsion. No additional surfactant is added, so no new particles are formed. Monomer is fed in and initiator is added. Polymerization occurs in the previously formed particles, so that each one grows as monomer diffuses to it and is converted (Fig. 5-10). When the seed monomer and added monomer are different, graft copolymers may be formed provided the dead polymer in the seed can react by means of residual unsaturation or chain transfer.

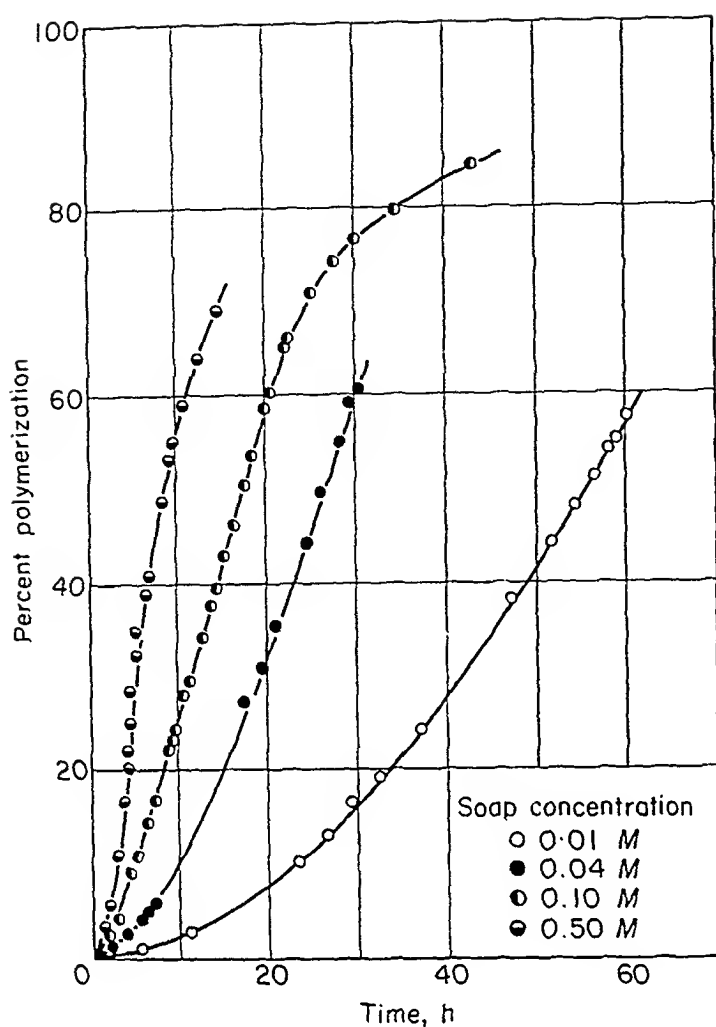
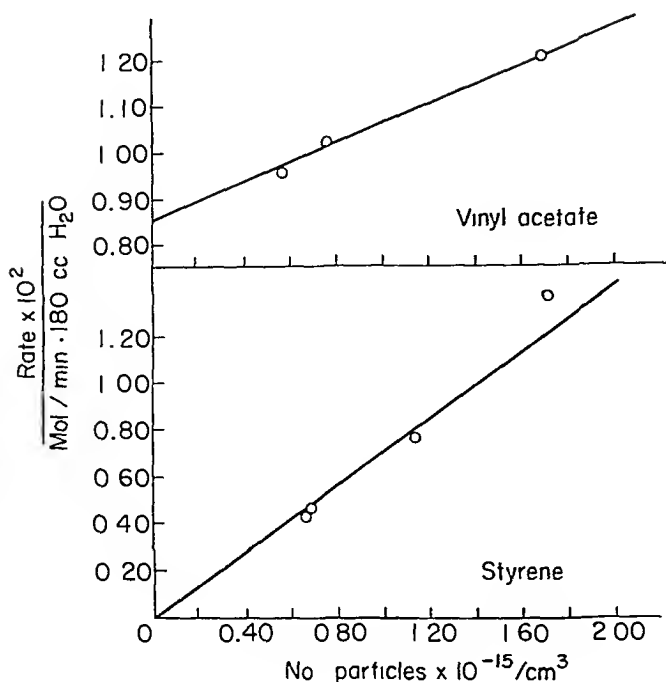


FIGURE 5-9

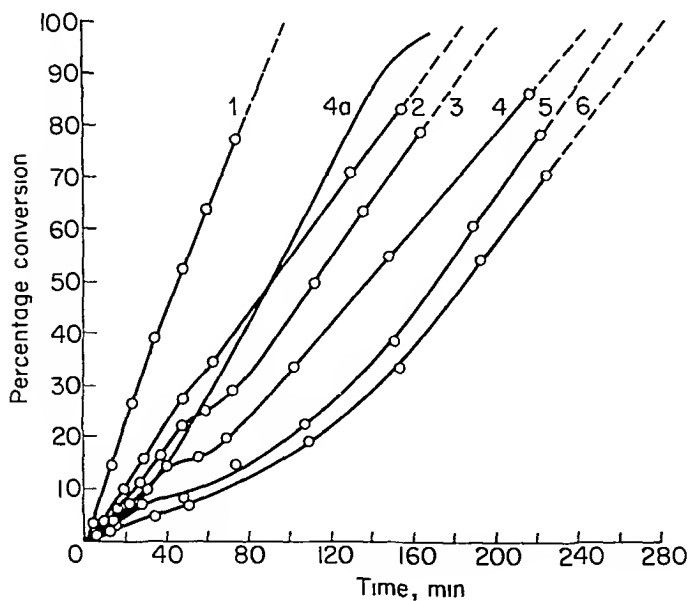
Polymerization of isoprene at 50°C for four concentrations of emulsifier (potassium laurate) [16].

A small amount of water solubility can alter the polymerization characteristics. Vinyl acetate dissolves in water only to the extent of 2%, but this is enough to give a combination of emulsion and solution polymerizations when emulsion polymerization is attempted (Fig. 5-10). The rate also is proportional to the initiator concentration [17]. Another exceptional case is vinylidene chloride, where monomer is almost insoluble in polymer but is adsorbed on the surface of polymer particles. Under these circumstances, faster stirring can accelerate the reaction (Fig. 5-11) [18].

The latex that results from emulsion polymerization may be the desired form for the intended end use. Some paints and adhesives can use latexes directly. However, if massive polymer is desired, recovery may involve coagulation by heating, freezing, salt or acid addition, spray drying, or mechanical turbulence. Surfactants, coagulants, and initiator fragments often remain as impurities in the final product under these circumstances. In the production of styrene-butadiene rubber (SBR), sodium soaps of fatty acids are used as emulsifiers. Acidification of the final latex simultaneously destroys the surfactant and deposits free fatty acid in the coagulum, where it is a valuable adjunct to the sulfur cross-linking reaction used later on for vulcanization.

**FIGURE 5-10**

Rate of polymerization of styrene and vinyl acetate vs. number of particles using a seed of poly(vinyl acetate) latex [17].

**FIGURE 5-11**

Effect of surfactant concentration on emulsion polymerization of vinylidene chloride at 36°C [18]. Initiator is 0.15 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and 0.15 g $\text{Na}_2\text{S}_2\text{O}_5$ /100 g monomer. Sodium lauryl sulfate concentration of (1) 10.0 g, (2) 5.0 g, (3) 3.0 g, (4 and 4a) 2.0 g, (5) 1.0 g, (6) 0.50 g/100 g monomer. Stirring rate of 285 rev/min except for 4a, which is 756 rev/min.

5-6 COMPARISON OF POLYMERIZATION METHODS

Bulk polymerization offers real hazards. The thermal conductivities of monomers and polymers are low, and viscosity buildup limits heat transfer by forced convection. Removal of unreacted monomer is difficult because of the low surface-to-volume ratio. On the other hand, the level of impurities can be held down by use of low initiator levels and diligent monomer removal.

Solution polymerization offers easier temperature control because of (1) added heat capacity of solvent and (2) lower viscosity. Removal of last traces of solvent and unreacted monomer can be difficult. Level of impurities can be very low, since the initiator residues can be washed out.

Temperature control is more convenient in *emulsion polymerization*, because the viscosity changes very little with conversion. Also, thermal conductivity and specific heat of water are higher than those for organic solvents. Removal of monomer can be accomplished without coagulating the latex. However, impurity levels are usually rather high because surfactant and coagulant residues are hard to remove. The agglomeration processes tend to give porous particles that trap some of the aqueous phase with its dissolved salts and surfactant.

Suspension polymerization is essentially a bulk polymerization carried out in droplets. Temperature control is complicated by the unstable nature of the suspension. Agitation is critical. Often, as the viscosity *within the beads* rises, the reaction rate increases suddenly (Trommsdorff effect). This leads to a surge in heat generation, which does not usually occur in solution or emulsion polymerization. On the other hand, the viscosity of the continuous phase (water) does not change during the reaction, so that control is easier than in bulk polymerization. Monomer recovery parallels that in emulsion polymerization. Polymer recovery is simple and usually leads to lower impurity levels than with emulsion polymers.

The differences in preparing polystyrene by several methods can be studied in Figs. 13-9 and 13-10.

Polymer processing after the reaction step varies with the solubility, the physical state, and the desired final form of the polymer, as well as with the extent of conversion of monomer to polymer. Coagulation of latexes and filtration of suspension polymers have been mentioned. Flow sheets for industrial processes in Chaps. 13 and 14 illustrate a wide variety of processing operations. Washing to remove catalyst residues, low-molecular-weight polymer, or atactic fractions may be practical for a polymer like polypropylene, which can be handled as a slurry of relatively hard particles. Recrystallization is a common procedure for low-molecular-weight organic compounds but not for polymers. Purification by dissolving and precipitation is avoided because of the expense involved with copious quantities of solvents. Even deionized water can be ruinously expensive if 100 volumes are used for a single volume of polymer. Most polymers recovered by precipitation separate as slimy, sticky masses that are hard to handle. Heating, cooling, and pumping viscous melts and solutions require the same attention to power input and surface scraping as polymerization design. Final removal of liquids, whether solvent, diluent, or unreacted monomer, is complicated by the high viscosities and low diffusivities characteristic of most polymers. Vacuum evaporators, latex strippers, and vented extruders are used, as well as belt, pan, spray, and rotary kiln types of dryers.

PROBLEMS

- 5-1. One kilogram of a 20% (by weight) solution of acrylamide in water at 30°C is polymerized adiabatically with a redox initiator. The peak temperature reached is 80°C. What is the molar heat of polymerization?
- Molecular weight (monomer) = 71
 Heat capacity (monomer and polymer) = 0.5 cal/g·°C
 Heat capacity (water) = 1.0 cal/g·°C
 Heat capacity of container, stirrer, etc. = 0.1 kcal/°C
- 5-2. (a) In what basic way is emulsion polymerization similar to suspension polymerization? (b) What advantage does this give over solution polymerization? (c) In what way do emulsion and suspension polymerizations differ basically? (d) In an unstirred, bulk polymerization that proceeds to 100% conversion, how can the effects of shrinkage and heat of polymerization be handled?
- 5-3. Why would one expect the apparent order (in monomer) of an emulsion polymerization to rise from zero after 80 or 90% conversion? What maximum value should it reach?
- 5-4. What order of rate dependence would be expected in a suspension polymerization initially? Why might the rate change abruptly after 5 to 20% conversion?
- 5-5. According to Fig. 5-10, the rate of emulsion polymerization for styrene varies directly with the number of particles at 60°C. Taking k_p (at 50°C) from Table 4-2, calculate the dynamic concentration of monomer in particles under these conditions. The experimental value of 5.2 mol/liter has been found by M. Morton et al. [19].
- 5-6. Company Y has available a 5% (by weight) latex of poly(methyl methacrylate) containing particles that average 0.40 μm in diameter. In order to grow these to a larger size, 8 kg of monomer will be fed into the latex per kilogram of polymer as polymerization proceeds without further addition of emulsifier. The reaction is carried on until all monomer is added to the reactor and the ratio of monomer to polymer in the reactor has decreased to 0.1. Then the unreacted monomer will be steam-stripped and recovered.

Estimate the time required for the reaction in hours, the rate of heat removal initially (watt/m³ of original latex), and the final particle diameter.

Data:

Isothermal reaction at 70°C

$H_p = -13.0$ kcal/mol (54.4 kJ/mol)

Density (polymer) = 1.2 g/cm³

Density (monomer) = 0.9 g/cm³

$k_p = 640$ liter/mol·s

Dynamic solubility of monomer in polymer = 1 g monomer/2 g polymer

- 5-7. In an emulsion polymerization, all the ingredients are charged at time $t = 0$. The time to convert various amounts of monomer to polymer is indicated in the following table. Predict the time for 30% conversion. Polymerization is "normal" (no water solubility or polymer precipitation).

Fraction of original charge of monomer converted to polymer	Time (h)
0.05	2.2
0.12	4.0
0.155	4.9

- 5-8. Propylene is polymerized in a slurry reactor by an equimolar mixture of aluminum triethyl and titanium tetrachloride. The catalyst residue remains with the polymer in a hydrolyzed form. If a customer specifies a maximum ash content of 0.10 wt % in product, what productivity (moles of monomer converted per mole of catalyst) must be achieved? Assume the ash is entirely Al_2O_3 and TiO_2 .
- 5-9. If 20,000 kg of vinyl chloride is polymerized in a 40-m^3 jacketed reactor with 25 m^2 of heat transfer area, what overall rate of heat transfer is needed when the reaction takes place in 6 h? If the jacket-side coefficient is $6000\text{ watt/m}^2\cdot^\circ\text{C}$ and the temperature difference is 40°C , what inside coefficient is necessary? Neglect wall resistance.
- 5-10. In an adiabatic tubular reactor, styrene is converted partially to polymer at high pressure and the mixture of monomer and polymer is sprayed into a vacuum chamber with evaporation of monomer and recovery of polymer. If the heat of vaporization is 355 J/g and the monomer enters the tube at 50°C , what fraction can be converted to polymer per pass and still allow polymer recovery at 50°C ?
- 5-11. Monomer A is polymerized at 80°C by two methods in two separate runs: (a) in an inert solvent (no chemical interactions), and (b) as an aqueous suspension. If the *initial* rate of polymerization for 1 liter of solution is 0.057 mol/h , what is the expected *initial* rate for 1 liter of suspension (in mol/h)?

	Solution (1 liter)	Suspension (1 liter)
Monomer	50 g (0.50 mol , 60 cm^3)	same
Benzoyl peroxide	$1.0 \times 10^{-3}\text{ mol}$ (negligible volume)	$1.0 \times 10^{-4}\text{ mol}$ (negligible volume)
Diluent	940 cm^3 of benzene	940 cm^3 of water
Additives	none	0.1 g of poly(vinyl alcohol)

- 5-12. Consider three 10-m^3 reactors operating at 70°C . Each contains 1000 kg of styrene monomer. Additional ingredients initially are:

	Reactor I	Reactor II	Reactor III
Inert liquid	8.00 m^3 benzene	8.00 m^3 water	8.00 m^3 water
Initiator	1.00 kg benzoyl peroxide	1.00 kg benzoyl peroxide	1.00 kg potassium persulfate
Polystyrene	10.0 kg polymer in solution	10.0 kg polymer (dissolved in the monomer)	10.0 kg polymer in stable latex form
Additive	—	1.00 kg poly(vinyl alcohol)	—

In each of the three reactors, does $-d[M]/dt$ (initial value) increase, decrease, or remain essentially the same when each of the following changes is made? Also predict the effect of each change on the x_n of the polymer being formed initially.

- Amount of initiator is doubled.
- Amount of monomer is halved.
- Temperature is increased to 90°C .
- Amount of initial polymer is doubled.

5-13. In a solution polymerization, heat removal may be complicated by an increase in viscosity as polymerization proceeds. For the following situation, the heat of polymerization can be handled initially by a temperature difference between contents and jacket of 20°C . What temperature difference is required when half the charge has been converted to polymer? Conditions are:

- (a) Initial charge of monomer is 100 kg/m^3 of solution.
- (b) The overall coefficient of heat transfer is $2000\text{ watt/m}^2\cdot^{\circ}\text{C}$ at the start of the reaction. It varies with viscosity of contents to the inverse one-third power.
- (c) $(\text{Viscosity of solution})/(\text{initial viscosity}) = \exp(0.05c)$ where c is the concentration of polymer in kg/m^3 .
- (d) The rate of polymerization changes with concentration according to Eq. (4-4) with initiator concentration held constant.

5-14. For the conditions of the previous problem, if the monomer is acrylamide, the solvent is water, and the time for 50% conversion is 35 min, what heat transfer area is required per cubic meter of solution?

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6

THE MOLECULAR WEIGHT OF POLYMERS

6-1 AVERAGE MOLECULAR WEIGHT

The high molecular weight of polymers is responsible for many of the properties that make polymers valuable as a class of materials. Although there is no sharp dividing line, we can draw an imaginary one at a molecular weight of about 2000, since that is near the limit of convenient purification by distillation or extraction. Also, differences between members of a homologous series differing in steps of 100 or so (the molecular weight of a typical monomer) become so slight as to prevent clean separations. Some polymers such as polyethylene, poly(ethylene oxide), and dimethyl silicones are commercially available in sizes ranging almost continuously from monomer or dimer up to molecular weights in the millions. Except for the smaller members of each series, each of these products is a mixture of different-sized molecules having an *average molecular weight*, which we can define and measure in several ways, and a *distribution* of molecular weights. Distributions usually have been rather tedious to measure and not as often specified as the average molecular weight. However, new analytical techniques are changing this situation.

If someone told you that he wanted to drop into your hand, from a height of 1 ft, a series of 1000 steel balls with an average diameter of 2.4 in, you might agree to help him in his playful experiment. After all, a 2.4-in-diameter ball weighs only about 2 lb. However, if he said the average diameter was 23.6 in, your attitude might be less cooperative. Both numbers could refer to the same series of balls, the difference being in the manner in which the "average" diameter is calculated. If the population is as shown in Table 6-1, we can calculate an average diameter in several ways:

The average diameter $\bar{D}_L$, based on length (one dimension):

$$\bar{D}_L = \frac{\sum N_i D_i}{\sum N_i} = \frac{2400}{1000} = 2.4 \text{ in}$$

TABLE 6-1
Hypothetical Distribution of Balls

Number of balls N_i	Diameter D_i , in	Length $N_i D_i$	Area ($\times 1/\pi$) $N_i D_i^2$	Volume ($\times 6/\pi$) $N_i D_i^3$
900	1	900	900	900
50	5	250	1,250	6,250
50	25	1250	31,250	781,250
$\Sigma N_i = 1000$		$\Sigma N_i D_i = 2400$	$\Sigma = 33,400$	$\Sigma = 788,400$

The average diameter $\bar{D}_A$, based on area (two dimensions):

$$\bar{D}_A = \frac{\Sigma N_i D_i^2}{\Sigma N_i D_i} = \frac{33,400}{2400} = 13.9 \text{ in}$$

The average diameter $\bar{D}_V$, based on volume (three dimensions):

$$\bar{D}_V = \frac{\Sigma N_i D_i^3}{\Sigma N_i D_i^2} = \frac{788,400}{33,400} = 23.6 \text{ in}$$

Although $\bar{D}_L$ reflects the preponderant number of small balls, the 1-in balls represent only about 0.1% of the total volume. $\bar{D}_V$ reflects the importance of the few large balls, which represent 99% of the volume (and weight) of the system. Incidentally, each 25-in ball weighs about 1 ton.

Let us now imagine a population of polymers with molecular weights distributed as in Table 6-1, where N is now the number of molecules of molecular weight $M = D$. The quantity we called $N_i D_i$ before is now $N_i M_i = W_i$, the weight of species with molecular weight M_i . We have used before the concept of a number-average molecular weight M_n , where

$$M_n = \frac{\text{total weight of system}}{\text{molecules in system}} \quad (6-1)$$

In terms of any population, then

$$M_n = \frac{\Sigma N_i M_i}{\Sigma N_i} = \frac{\Sigma W_i}{\Sigma (W_i/M_i)} \quad (6-2)$$

As in the case of the steel balls, M_n is very sensitive to the concentration of low-molecular-weight species. The weight-average molecular weight M_w is defined as

$$M_w = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i} = \frac{\Sigma W_i M_i}{\Sigma W_i} \quad (6-3)$$

In correlating such important polymer properties as viscosity or toughness, M_w often is a more useful parameter than M_n . Higher averages are defined as

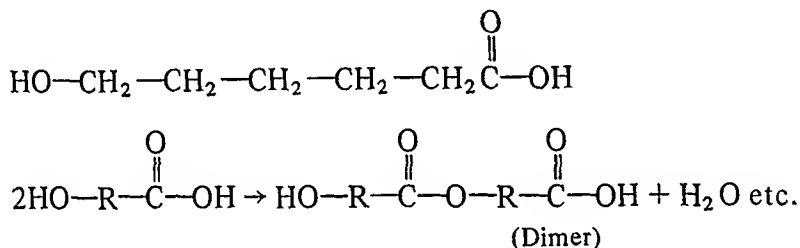
$$M_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2} = \frac{\sum W_i M_i^2}{\sum W_i M_i} \quad (6-4)$$

$$M_{z+1} = \frac{\sum N_i M_i^4}{\sum N_i M_i^3} = \frac{\sum W_i M_i^3}{\sum W_i M_i^2} \quad (6-5)$$

These are used less often than M_n and M_w . The ratio of M_w to M_n is a measure of the broadness of a distribution, since each is influenced by an opposite end of the population. The quantity M_w/M_n is the *polydispersity index*.

6-2 THEORETICAL DISTRIBUTIONS

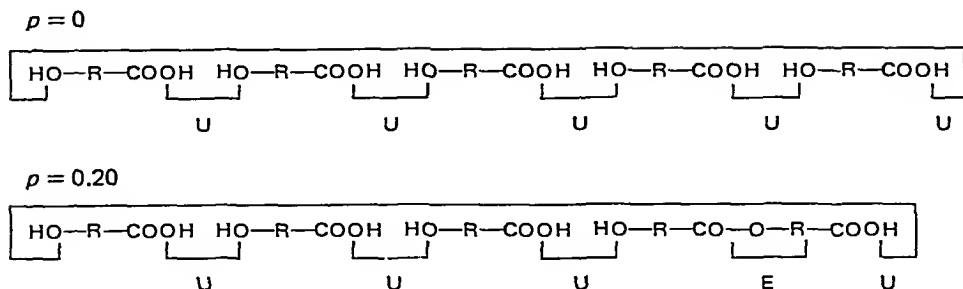
With the possible exception of some naturally occurring proteins, all polymers are mixtures of many molecular weights ("polydisperse"). This is a consequence of the random nature of polymerization reactions. For example, take the case analyzed by Flory [1] in which the monomer is an ω -hydroxy acid (see also Sec. 4-5).



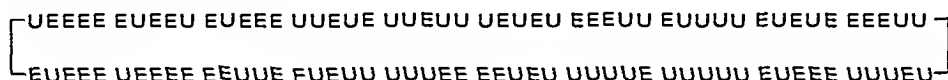
This is a typical stepwise polymerization in which each successively higher molecular weight, dimer, trimer, etc., is just as reactive as monomer. An important parameter is the fraction converted, p . If we have a population of such monomers, each can react to form an ester group. Each esterification eliminates one carboxyl and one hydroxyl group. With five monomers (Fig. 6-1) there would be a maximum of five esterifications ($p = 1$). Initially, p is 0. After one reaction, $p = 0.20$. Abbreviating the unreacted sites by the symbol U and the esterified sites by the symbol E , we can generate a distribution of molecular weights by random reaction of 50 out of 100 sites ($p = 0.5$). If we had alternated sites of reaction with unreacted sites, we would have generated 50 dimers and no other species. Another possible extreme would be to generate 49 monomers and 1 polymer molecule with a degree of polymerization x of 51. We have 50 molecules in either case. With random reaction (Fig. 6-1), monomers predominate in number of molecules N_x , although not necessarily in weight xN_x . If our sample population were much larger, as it is in any macroscopic polymerization, we could assign a probability $(P_r)_x$ that a monomer unit selected at random is a part of a polymer with degree of polymerization x . We expect this to be a function of p , which is the probability that any particular reactive site has been esterified. The probability that a monomer unit is still unreacted varies from 1 when $p = 0$ to 0 when $p = 1$. We surmise that

$$(P_r)_1 = 1 - p \quad (6-6)$$

Population of five monomers



Population of 100 monomers



Summary:

	x	N_x	xN_x
Monomer (—UU—)	1	25	25
Dimer (—UEU—)	2	15	30
Trimer (—UEEU—)	3	2	6
Tetramer (—UEEEU—)	4	4	16
Pentamer (—UEEEUU—)	5	2	10
Hexamer (—UEEEEEU—)	6	1	6
Heptamer (—UEEEEEUU—)	7	1	7
		50	100

FIGURE 6-1

Generation of molecular weight distribution by random reaction.

The likelihood that a unit has become part of a dimer is p times $(P_r)_1$. Each additional unit is less likely, since the cumulative probability is represented by a product of the probabilities of each step. Thus we see that

$$(P_r)_x = (1 - p)p^{x-1} \quad (6-7)$$

Also,

$$\sum_{x=1}^{\infty} (P_r)_x = \sum_{x=1}^{\infty} (1 - p)p^{x-1} = 1 \quad (6-8)$$

Now we can call $(P_r)_x$ the *mole fraction of x-mer*, since it is a normalized probability (i.e., the summation over all values of x is unity). According to Eq. (6-7), the degree of polymerization with the largest mole fraction *always* is 1, namely, monomer. Keep in mind that we are dealing with a particular polymerization scheme in which all species are at equilibrium. The number-average degree of polymerization $\bar{x}_n$ for a distribution represented by Eq. (6-7) is

$$x_n = \frac{\text{number of monomer units originally charged}}{\text{number of molecules in system}} = \frac{1}{1-p} \quad (6-9)$$

Disregarding the contribution to molecular weight made by the end groups, the *molecular weight* of a polymer M is related to the *degree of polymerization* x by

$$M = M_0 x \quad (6-10)$$

where M_0 is the molecular weight of a monomer unit in the chain. We can write Eq. (6-7) for x and for x_n and combine the two to give

$$\ln \frac{(P_r)_x}{(P_r)_{x_n}} = (x - x_n) \ln p \quad (6-11)$$

But $-\ln p \cong 1 - p = 1/x_n$, so that

$$\ln \frac{(P_r)_x}{(P_r)_{x_n}} \cong 1 - \frac{x}{x_n} \quad (6-12)$$

This "normalized" equation for mole fraction as a function of degree of polymerization is shown in Fig. 6-2.

A second kind of average degree of polymerization can be defined as

$$x_w = \frac{\sum W_x x}{\sum W_x} \quad x = 1, 2, 3, \dots \quad (6-13)$$

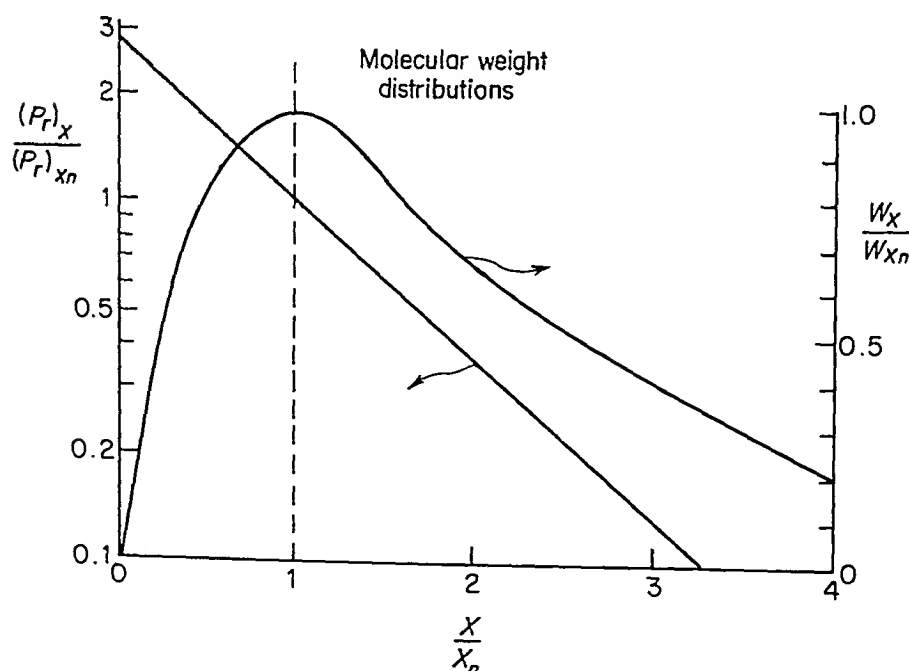


FIGURE 6-2
Normalized distributions according to Eqs. (6-12) and (6-17).

where W_x is proportional to the weight of x -mer and x_w is the *weight-average degree of polymerization*. The weight of x -mer from Eq. (6-7) is

$$W_x = x(1-p)p^{x-1}M_0 \quad \text{and} \quad \Sigma W_x = \frac{M_0}{1-p} \quad (6-14)$$

Thus we have

$$x_w = \frac{\Sigma (P_r)_x x^2}{\Sigma (P_r)_x x} = \frac{\Sigma x^2(1-p)p^{x-1}}{\Sigma x(1-p)p^{x-1}} = \frac{1+p}{1-p} \quad (6-15)$$

The weight fraction of x -mer w_x is given by

$$w_x = \frac{W_x}{\Sigma W_x} = x(1-p)^2 p^{x-1} \quad (6-16)$$

As in Eq. (6-12), we can have a "normalized" distribution:

$$\ln \frac{w_x}{w_{x_n}} = \ln \frac{x}{x_n} + (x - x_n) \ln p \cong \ln \frac{x}{x_n} - \frac{x}{x_n} + 1 \quad (6-17)$$

This also is plotted in Fig. 6-2. Higher averages of degree of polymerization are sometimes useful:

$$x_z = \frac{\Sigma (P_r)_x x^3}{\Sigma (P_r)_x x^2} \quad (6-18)$$

$$x_{z+1} = \frac{\Sigma (P_r)_x x^4}{\Sigma (P_r)_x x^3} \quad (6-19)$$

What we have been describing is sometimes called the *most-probable distribution*. It gives $x_w/x_n = 1 + p$. The ratio of 2 when p approaches unity is found experimentally for many stepwise and also for many chain polymerizations, although the reasoning can be different. Under conditions of chain polymerization with all polymers initiated and growing *simultaneously*, the distribution can be much narrower. For example, in a butyl-lithium-initiated polymerization to give living polymers, the simultaneous growth of polymer chains gives a Poisson distribution [2].

$$(P_r)_x (\text{mole fraction of } x\text{-mer}) = \frac{e^{1-x_n}(x_n-1)^{x-1}}{(x-1)!} \quad (6-20)$$

$$\text{or} \quad \ln (P_r)_x = 1 - x_n + (x-1) \ln (x_n-1) - \ln [(x-1)!] \quad (6-21)$$

$$w_x (\text{weight fraction of } x\text{-mer}) = \frac{x(P_r)_x}{x_n} \quad (6-22)$$

$$\frac{x_w}{x_n} = 1 + \frac{x_n - 1}{x_n^2} \quad (6-23)$$

It can be seen that even when x_n is small, say about 10, x_w/x_n is nearly unity. Polymers can be produced on a commercial scale with

$$\frac{M_w}{M_n} = \frac{x_w}{x_n} < 1.1$$

by using butyl lithium as the initiator.

We can further illustrate the differences in the various averages by examining the sample of Fig. 6-1 (Table 6-2). In this example, monomer ($x = 1$) has the highest mole fraction but not the highest relative weight (W_x). The average degrees of polymerization are also calculated according to the equations presented. As mentioned before, the usefulness of each of these numbers may depend on the particular property we are looking at. The reactivity of a urethane prepolymer may depend entirely on x_n . On the other hand, the viscosity of a polymer melt often varies more directly with x_w .

6-3 EMPIRICAL DISTRIBUTION MODELS

The distribution of molecular weights has been shown to be important in many diverse applications including flow of melts and solutions, aging and weathering behavior, adhesion, and flocculation. Because of the difficulties involved in measuring a distribution in detail, one shortcut has been to postulate a reasonable mathematical form or model for the distribution and then evaluate the parameters from x_n and x_w [3]. In general, such a model would give w_x , the weight fraction of x -mer, as a function of

TABLE 6-2
Analysis of Distribution From Fig. 6-1

Degree of polymerization x	Number of moles N_x	Mole fraction $P_r = N_x/\Sigma N_x$	Relative number of monomer units in x -mer $W_x/M_0 = x(P_r)_x$	Weight fraction $w_x = W_x/\Sigma W_x$		
				w_x	xw_x	x^2w_x
1	25	0.50	0.50	0.25	0.25	0.25
2	15	0.30	0.60	0.30	0.60	1.20
3	2	0.04	0.12	0.06	0.18	0.54
4	4	0.08	0.32	0.16	0.64	2.56
5	2	0.04	0.20	0.10	0.50	2.50
6	1	0.02	0.12	0.06	0.36	2.16
7	1	0.02	0.14	0.07	0.49	3.43
	50	1.00	2.00	1.00	3.02	12.64

$$x_n = \frac{\Sigma x(P_r)_x}{\Sigma (P_r)_x} = \frac{2.00}{1.00} = 2.00$$

$$x_w = \frac{\Sigma x^2(P_r)_x}{\Sigma x(P_r)_x} \quad \text{or} \quad \frac{\Sigma xw_x}{\Sigma w_x} = \frac{3.02}{1.00} = 3.02$$

$$x_z = \frac{\Sigma x^3(P_r)_x}{\Sigma x^2(P_r)_x} \quad \text{or} \quad \frac{\Sigma x^2w_x}{\Sigma xw_x} = \frac{12.64}{3.02} = 4.19$$

x , x_w , x_n , and perhaps other parameters. The "most-probable" distribution, Eq. (6-7), has only one parameter p , which can be evaluated from either x_n [Eq. (6-9)] or x_w [Eq. (6-15)]. If the experimentally determined ratio of x_w/x_n is not nearly 2 for high-molecular-weight material, the model cannot be used. The Schulz distribution is a more general form of the most-probable:

$$w_x = \frac{a}{x_n \Gamma(a+1)} \left(\frac{ax}{x_n} \right)^a \exp \left(-\frac{ax}{x_n} \right) \quad (6-24)$$

where $x_w/x_n = (a+1)/a$ and $\Gamma(a+1)$ is the gamma function of $a+1$. When $a=1$ and x is large, this becomes the same as the most-probable since $x_n = 1/(1-p)$ and $(x-1) \ln p \cong -x/x_n$. However, any value of x_w/x_n can be inserted. Qualitatively, the curves will resemble Fig. 6-2 except that the overall breadth will reflect the influence of the polydispersity index x_w/x_n .

It will be seen in the next section that some experimental methods of measuring distribution result in a cumulative distribution function $W(x)$, from which the differential distribution $w_x = dW/dx$ can be derived. We are speaking now of distributions in the higher ranges of x_n , where the approximation $\Sigma w_x = \int w_x dx$ is applicable. It has been observed that a plot of $W(x)$ against x on logarithmic probability paper often gives a straight line. In terms of w_x this becomes the Wesslau distribution:

$$w_x = \frac{1}{\beta \pi^{1/2}} \frac{1}{x} \exp \left(-\frac{1}{\beta^2} \ln^2 \frac{x}{x_0} \right) \quad (6-25)$$

where $\beta^2 = \ln(x_w/x_n)^2$ and $x_0 = x_n \exp(\beta^2/4)$. Once again, specification of x_w and x_n defines the entire distribution. As with the Schulz model, only the central value of the distribution, reflected by x_n , and the breadth, measured by x_w/x_n , can be changed. On a cumulative weight [$W(x)$] basis, the Schulz and Wesslau models give similar curves (Fig. 6-3). On a differential (w_x) basis, qualitative differences become

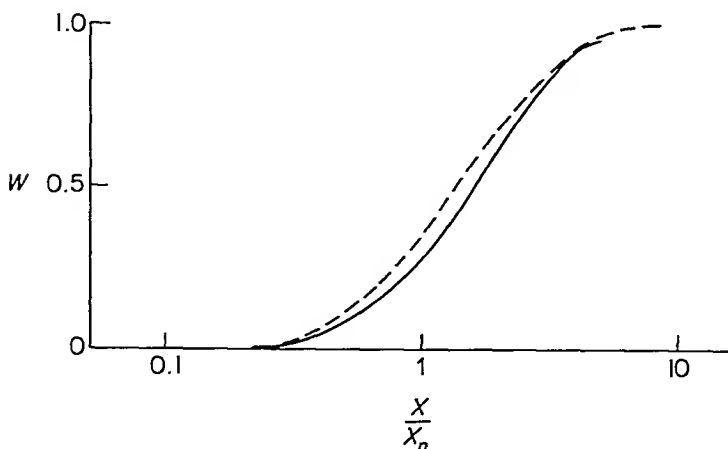


FIGURE 6-3

Cumulative weight fraction W as a function of ratio of degree of polymerization to number-average value for Schulz (solid line) and Wesslau (dashed line) models.

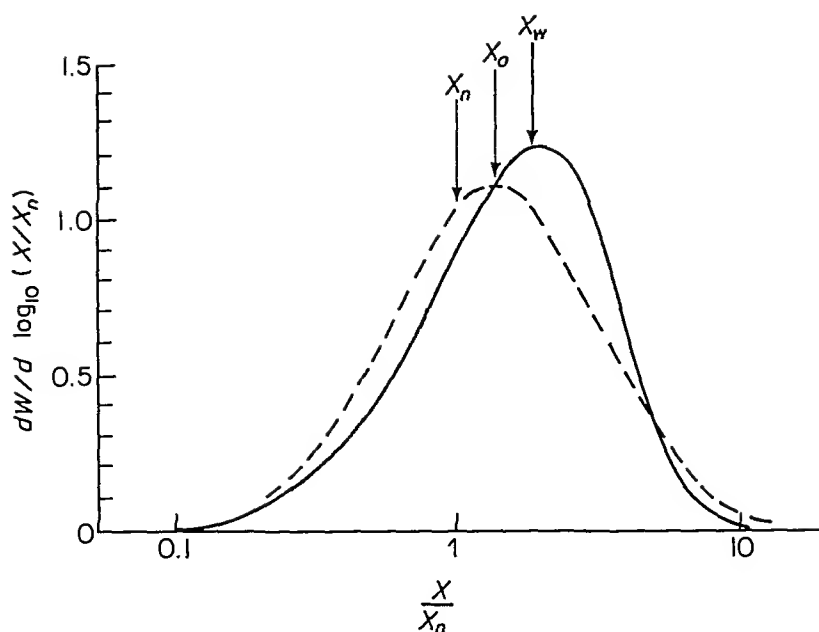


FIGURE 6-4
Differential distribution curves for models of Fig. 6-3.

apparent (Fig. 6-4). When dealing with high molecular weights ($x > 100$), it becomes convenient to treat distributions as being continuous rather than finite. As an example, let us assume that the cumulative weight fraction $W(x)$ of a polymer with degree of polymerization less than x is given by

$$\begin{aligned} W(x) &= 0.01(x - 10) && \text{for } 10 < x < 110 \\ W(x) &= 0 && \text{for } x < 10 \\ W(x) &= 1 && \text{for } x > 110 \end{aligned} \quad (6-26)$$

The *differential* weight distribution w_x then is

$$w_x = \frac{dW(x)}{dx} = 0.01 \quad (6-27)$$

The degree of polymerization is obtained by integration and normalization.

$$x_n = \frac{\int_1^\infty w_x dx}{\int_1^\infty w_x/x dx} = \frac{\int_{10}^{110} 0.01 dx}{\int_{10}^{110} 0.01/x dx} = 41.7 \quad (6-28)$$

$$x_w = \frac{\int_1^\infty xw_x dx}{\int_1^\infty w_x dx} = \frac{\int_{10}^{110} 0.01x dx}{\int_{10}^{110} 0.01 dx} = 60.0 \quad (6-29)$$

The continuous models are particularly useful when analyzing experimental data on distributions where a cumulative weight is obtained first and must be converted mathematically to a differential distribution.

6-4 MEASUREMENT OF DISTRIBUTION

Both x_n and x_w can be measured independently (Secs. 6-6 and 6-7) in order to get some idea of polydispersity. The ultracentrifuge, when applicable, gives a distribution directly. However, until the advent of gel permeation chromatography, fractionation of polymer from dilute solution was used. Usually there is a decrease in solubility with increasing molecular weight. Polymer can be put in dilute solution and progressively precipitated by addition of increments of a nonsolvent [4]. The nonsolvent is added to give a visible precipitate. Then the system is heated to a temperature at which it is homogeneous, after which it is slowly cooled over a period of hours to a standard temperature. A variation is to cool the solution to successively lower temperatures and separate a fraction at each temperature rather than at each increment of nonsolvent. The polymer-rich phase that separates, the so-called *coacervate*, usually is a small volume compared to the total volume of the system and is viscous or gelatinous. One drawback of this process of coacervation is that low-molecular-weight polymer is occluded in the coacervate even under conditions of slow cooling. Since this is more serious with higher molecular weights and with higher starting concentrations, a rule of thumb may be employed that the beginning concentration should be less than 1% polymer regardless of molecular weight and also that the concentration times the intrinsic viscosity (Sec. 7-4) should be less than 1. Another scheme is to redissolve each fraction and reprecipitate it under the same conditions of solvent-nonsolvent ratio and temperature. Figure 6-5 shows the relationship between the degree of polymerization of material remaining in solution and solvent composition when poly(vinyl

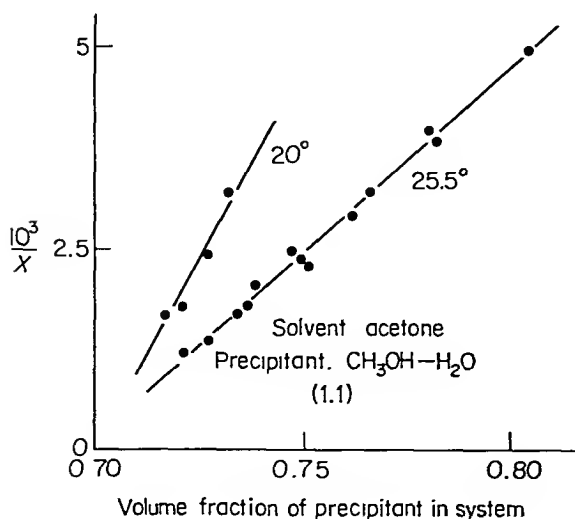


FIGURE 6-5

Decrease in solubility of poly(vinyl acetate) with added nonsolvent, increasing degree of polymerization x , and decreasing temperature [5].

TABLE 6-3
Analysis of Typical Fractionation Data

Raw experimental data			Calculated results		
Fraction no. i	Fraction of total weight recovered w_i	Degree of polymerization $x_i (\times 10^{-3})$	Σw_i	$\Sigma w_{i-1} + w_i/2$ $\bar{w}_i$	$(dW/dx)_i$ ($\times 10^3$)
1	0.050	1.1	0.050	0.025	0.040
2	0.100	2.5	0.150	0.100	0.060
3	0.120	4.1	0.270	0.210	0.063
4	0.083	5.8	0.353	0.313	0.052
5	0.075	7.4	0.428	0.390	0.043
6	0.110	9.4	0.538	0.483	0.039
7	0.120	12.5	0.658	0.598	0.030
8	0.130	17.5	0.788	0.723	0.0165
9	0.130	29.0	0.918	0.853	0.0072
10	0.082	64.0	1.000	0.959	0.0013

acetate) is precipitated from an acetone solution by addition of a methanol-water mixture.

The procedure is tedious, because hours or days are required for clean separation of each fraction. Even then, each fraction is heterogeneous with $x_w/x_n = 1.05$ to 1.2 at best. Rather than precipitate the polymer from a dilute solution, it is possible to dissolve a solid polymer fractionally [6]. Diffusion through the solid is slow, so it is essential that the material be spread out in a very thin film. A typical technique for fractionating polyethylene uses a 2-in-diameter column about 2 ft long packed with ordinary sand (40 to 200 mesh). A hot solution of polyethylene in xylene is introduced and cooled so that the entire charge of polymer, a few grams, is precipitated on the surface of the sand, giving a thin film. Then a solvent or a solvent mixture is added to elutriate the low-molecular-weight portion of the polymer. When no more polymer is elutriated at that solvent composition or temperature, the solvent-to-nonsolvent ratio is increased or the temperature is raised so that a higher molecular weight fraction can be extracted. Columns of this type can be automated with a few solenoid-operated valves and a fraction collector in order that fractionation of a sample into 10 to 20 fractions can be carried out overnight without immediate supervision. In this column method one does not have to wait for gravitational settling out of co-acervate, and it is the speed with which fractionation can proceed that is its advantage.

Both in precipitation and dissolving, a single equilibrium stage of separation is achieved. Multistaged separations are not usually convenient. In either case, the raw data consist of a series of i fractions each of weight w_i and an average molecular size $\bar{x}_i$. A cumulative curve can then be plotted in which the ordinate is $\Sigma w_{i-1} + w_i/2$ and the abscissa is $\bar{x}_i$. A smooth line through the points gives a curve that is a good approximation to $W(x)$, the cumulative molecular weight distribution function. Differentiation of this curve then gives $w_x = dW(x)/dx$, the differential molecular weight distribution function. The reason that the raw values of w_i and x_i cannot be plotted as a histogram is that the intervals of neither variable are uniform. An example (Table 6-3,

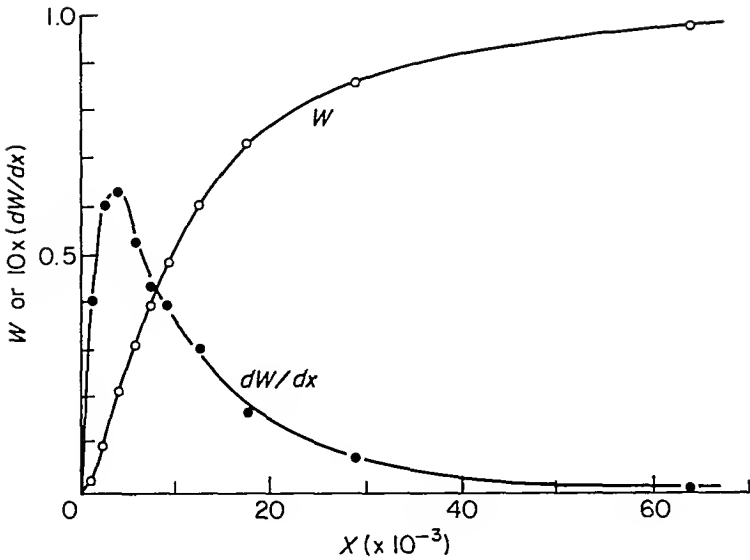


FIGURE 6-6
Differential and cumulative weight fraction plotted against degree of polymerization for distribution of Table 6-3.

Fig. 6-6) shows the long high-molecular-weight tail typical of most polymers. The uncertainty in the slope at the high end also is apparent. In Fig. 6-7 the advantage of a logarithmic plot in showing greater symmetry is seen.

A packed column technique is now popular under the names “gel filtration” and “gel permeation chromatography” (GPC). The first name was applied by Flodin and coworkers [7] to the separation obtained when water-soluble polymers are eluted from a column packed with swollen, cross-linked, hydrophilic dextran (Sephadex) beads. The second name was attached by Moore [8] to the separation of organic-soluble polymers in columns packed with swollen, cross-linked, lyophilic polystyrene beads. Both names are misleading, since the gel is not necessary, porous glass beads being equally applicable; filtration is not part of the process, small molecules being retarded and large ones passed rather than the other way around; and chromatography

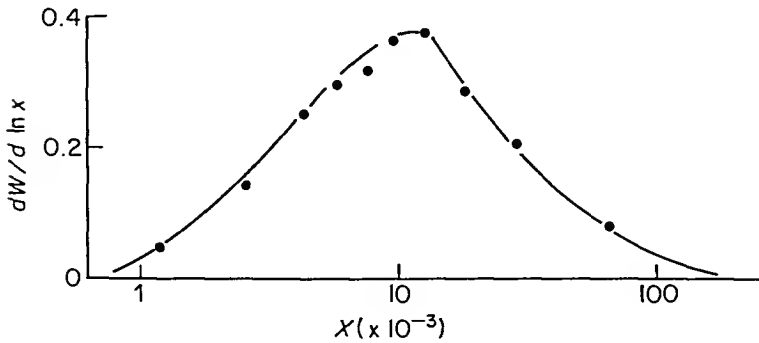


FIGURE 6-7
Data of Table 6-3 plotted as differential distribution on a logarithmic basis.

classically implies formation of colors, which seldom occurs in either technique. The term *liquid exclusion chromatography* has been recommended.

The principle of the method is illustrated in Fig. 6-8, where a mixture of small and large molecules has been deposited at one end of a column packed with porous beads. Initially there is a concentration gradient causing diffusion of polymer into the bead. However, the large molecules cannot penetrate the beads. A continuous flow of solvent sweeps the large molecules along and reverses the concentration gradient for the small ones so that they now diffuse back out of the beads. This process is repeated again and again as the sample is carried through the column. Eventually, when the sample is elutriated from the other end, large molecules will emerge first and the small ones, retarded by the diffusion in and out of the packing, will emerge last. This is just the opposite from what adsorption or filtration would have accomplished as in gas chromatography. When porous glass beads (about 100 mesh) are used as packing, the pore sizes can be measured by mercury intrusion. Pore diameters of 10 to 250 nm are useful for polymers in the 10^3 to 10^7 molecular weight range. Under conditions of constant temperature, flow rate, and concentration, for the same physical system, the retention volume V_r , the volume of solvent that must be elutriated from the system between the time the sample is introduced and the time it appears in the effluent, is a function only of the molecular size of the polymer. A calibration curve can be made for each individual polymer species by injecting samples of known molecular weight M and measuring $V_r(M)$ for each. A semilogarithmic plot (Fig. 6-9a) often has a straight portion. The molecular weight distribution of a new sample can be estimated by the relative concentration of polymer at each effluent volume, which now corresponds to a known molecular weight (Fig. 6-9b and c). Some workers have found that calibration curves in which $M[\eta]$ is plotted against V_r coincide for poly-

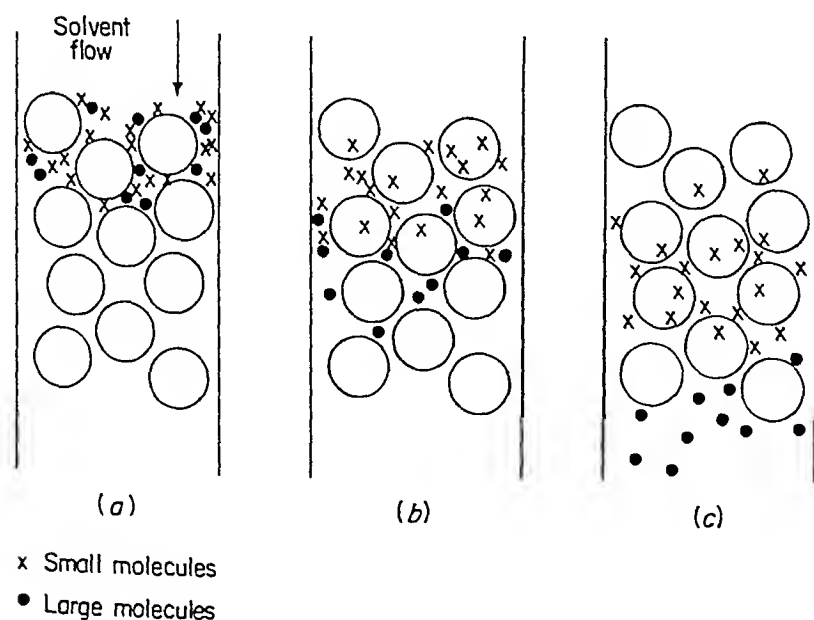


FIGURE 6-8

Process of gel permeation chromatography [10]. (a) Sample injection; (b) elution; and (c) continued elution.

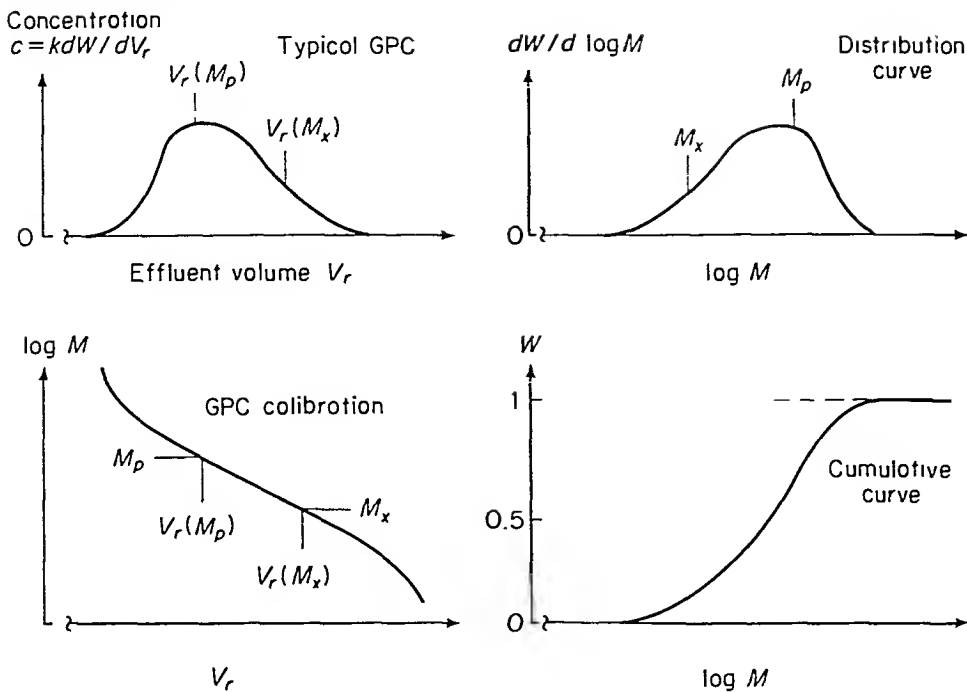


FIGURE 6-9
Stages in treatment of GPC data [9].

mers that differ in branching or in composition, thus giving a “universal” calibration. The quantity $[\eta]$, the intrinsic viscosity, is discussed in Sec. 7-4.

A typical system is shown in Fig. 6-10. The packed column may be anywhere from 1 to 20 ft long and packed with swollen beads, which leave about 30 to 50% void space. Solvent flows continuously by gravity or constant-volume pumping through the

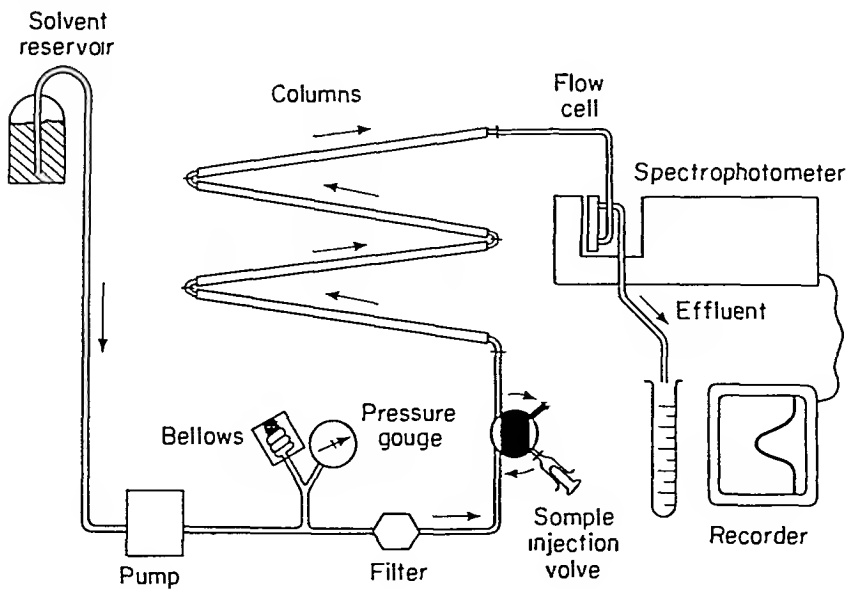
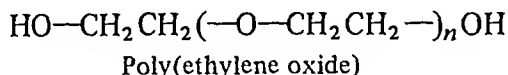


FIGURE 6-10
GPC apparatus [10].

column and then to an analyzer. Samples can be collected and concentration analyzed by various means, or a continuous-flow cell may be used to measure some property that can be correlated with concentration, such as conductivity, radioactivity, light absorbance, or refractive index. Infrared absorbance as a measure of concentration adds another dimension to the distribution analysis, because one can choose a band in the infrared region specific to one functional group and therefore to one component in a mixture or in a copolymer. For example, the ratio of hydroxyl to ether group in poly(ethylene oxide) varies with the molecular size. By measuring the concentration of hydroxy and ether



groups in the effluent from successive runs in the same system, the ratio of hydroxyl to ether, and therefore the molecular size, is obtained directly (Fig. 6-11). The distribution of a monomer within a copolymer distribution can also be measured by this technique.

In a conventional apparatus for liquid exclusion chromatography, a single high-molecular-weight sample usually can be analyzed in about two hours. In the 1970s it was found that shorter columns, finer packing, and much higher pressures lead to faster analyses, so that the time could approach 15 or 20 min per sample. In HPLC (high-performance liquid chromatography), pressures on the order of 100 atm often are used, compared to the 1 to 10 atm used in conventional GPC or gel filtration. Although similar to GPC in principle, HPLC requires precision, constant-flow-rate pumps, and special sample injection ports because of the small volumes and high pressures involved. In any chromatographic method the eluting liquid can be pro-

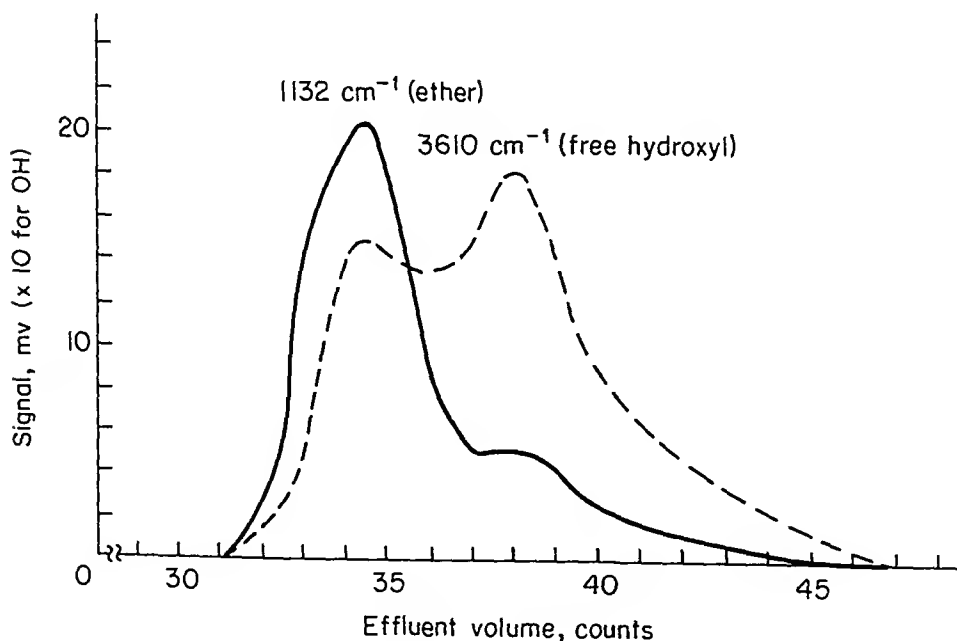


FIGURE 6-11

Mixture of poly(ethylene oxide)s with molecular weights of 300 and 4000 analyzed at ether and end group wave numbers (maximum signal for OH, 1.8 mV) [11].

grammed to change in temperature or in composition over the total analysis time. Such methods are not as commonly used in measuring molecular weight distribution as they are in analyzing mixtures of drugs, natural products, or other complex materials.

6-5 MEASUREMENT OF MOLECULAR WEIGHT

We accept nowadays as the valid indication of molecular size the molecular weights of polymers measured by the same techniques that have been used for small molecules. Before the 1920s, many chemists were reluctant to believe that such large, covalently bonded structures were possible. The molecular weights were regarded as "apparent" values brought about by a physical association of smaller molecules in a "colloidal" state. Perhaps we should not dismiss all the reservations that those scientists had when we look at experimental results. No measurement is foolproof, and it is a brave person indeed who lists a molecular weight of a polymer in the hundred-thousand range to four or five figures. Even the so-called absolute methods we are about to discuss depend on extrapolations that are not completely objective, since some mathematical model or form invariably must be postulated.

Methods for determining molecular weight can be *relative* or *absolute*. Many properties of polymers that depend on molecular weight, such as solubility, elasticity, adsorption on solids, and tear strength, can be correlated with an average molecular weight. Once correlated, the property can be used as a measure of molecular weight. In practice, viscosity of melts and dilute solutions is the most often used *relative* method (see Sec. 7-4). Absolute methods can be categorized by the kind of average they measure.

6-6 NUMBER-AVERAGE MOLECULAR WEIGHT METHODS

The measurement of the concentration of end groups when one knows the exact number per molecule is a method of counting the number of molecules. In the hydroxy-acid ester example, a simple titration by standard sodium hydroxide would give the total number of free carboxyl groups. Since there is but one such group for each polymer molecule, we have a molecule-counting method. End group counting can be more sophisticated, as in the use of infrared or isotopic analysis. In any of these we derive a number-average molecular weight M_n from Eq. (6-9) together with Eq. (6-10):

$$M_n = x_n M_0 \quad (6-30)$$

where M_0 is the molecular weight of a repeating unit in the polymer.

The magnitude of the depression of the melting point or the elevation of the boiling point of a solvent by a nonionized solute depends on the number of solute molecules present but not on their chemical nature. These *colligative* properties are used to estimate the molecular weight of a solute. The melting point depression is widely used in organic chemistry for the characterization of small molecules. The lowering of the melting temperature, $T_f - T$, is related to the normal melting tempera-

ture of the solvent T_f , its heat of fusion ΔH_f , and molecular weight M_1 , and also to the molecular weight of the solute M_2 and the relative weights of solvent and solute w_1 and w_2 , respectively [12]

$$T_f - T = \frac{RT_f^2}{\Delta H_f} \frac{M_1}{M_2} \frac{w_2}{w_1} \quad (6-31)$$

where R is the gas constant. For a solution of 1 g of polyethylene with $M_2 = 500$ in 100 g of camphor ($T_f = 178.4^\circ\text{C}$, $\Delta H_f = 2.58$ kcal/mol, $M_1 = 152$), $T_f - T$ is 0.48°C . As the molecular weight of the solute increases, measurement of the temperature lowering demands more sensitive equipment. In order to measure the number of molecules by colligative methods, it is necessary to use dilute solutions. In practice, we often extrapolate results to infinite dilution by some suitable linearization techniques. Osmotic pressure is a useful measuring method. We place on opposite sides of a semi-permeable membrane (typically cellophane) a polymer solution and pure solvent (Fig. 6-12). The membrane is selected to pass solvent but not polymer, the diffusion rate of polymer above some low molecular weight being negligibly small. To establish equilibrium, the pressure on the solution side must be greater. Either by waiting for equilibrium or by measuring and compensating for pressures automatically, osmotic pressure π can be measured at several concentrations. According to thermodynamic theory:

$$\left(\frac{\pi}{c}\right)_{c=0} = \frac{RT}{M} \quad (6-32)$$

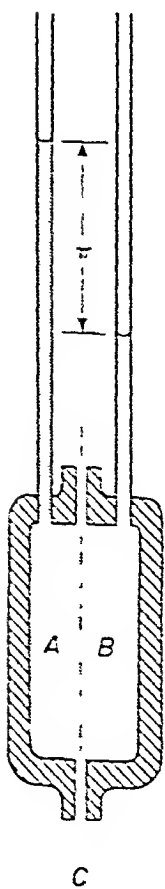


FIGURE 6-12
Osmotic pressure cell containing polymer solution A and solvent B separated by semipermeable membrane C. The osmotic pressure is π .

where π = osmotic pressure (g/cm^2) = $h\rho$

h = difference in liquid levels at equilibrium, cm

ρ = density of solvent, g/cm^3

c = concentration, g/cm^3

T = absolute temperature, K

M = molecular weight, g/mol

R = gas constant, 8.48×10^4 g·cm/mol·K

The difference between osmotic pressure and vapor pressure lowering can be illustrated by considering a situation where we take pure solvent at total pressure $P(0)$, increase the vapor pressure by increasing the total pressure to $P(0) + \pi$, then decrease the vapor pressure by adding a solute with a mole fraction N_2 (Table 6-4). Assuming ideal solutions and perfect gases, the criterion for equilibrium of solvent between the first and last conditions reduces to having the vapor pressure of solvent p in pure solvent at $P(0)$ equal to that in solution at $P(0) + \pi$. The change in vapor pressure of solvent with total pressure $P(T)$ is given by the Poynting equation [13]

$$\frac{dp}{dP(T)} = \frac{V_1}{V_g} \quad (6-33)$$

where V_1 is the molar volume of liquid solvent and V_g is the molar volume of gaseous solvent. Assuming a perfect gas, we can replace V_g by RT/p and integrate:

$$RT \int_{p(0)}^{p(\pi)} d(\ln p) = V_1 \int_{P(0)}^{P(0) + \pi} dP(T) \quad (6-34)$$

$$RT \ln \frac{p(\pi)}{p(0)} = V_1 \pi \quad (6-35)$$

where the vapor pressure is increased as indicated by the limits when the total pressure is increased by the osmotic pressure π . The subsequent decrease in vapor pressure is accomplished by adding solute according to Raoult's law, $p(N_2, \pi) = N_1 p(0, \pi)$. Our final condition is that $P(N_2, \pi)$ be equal to $p(0)$. Also, when N_1 is nearly 1, $-\ln N_1$ can be approximated by $1 - N_1$, which is N_2 , the mole fraction of solute. If we

TABLE 6-4
Characterization of Osmotic Pressure*

Condition	A	B	C
Mole fraction of solvent	1.0	1.0	N_1
Mole fraction of solute (polymer)	0	0	N_2
Vapor pressure of solvent	$p(0, 0)$	$p(0, \pi)$	$p(N_2, \pi)$
Total pressure on system	$P(0)$	$P(0) + \pi$	$P(0) + \pi$

*Criterion for equilibrium between A and C: $p(0, 0) = p(N_2, \pi)$ when partial molar free energy of solvent is same in A and B. Raoult's law: $p(N_2, \pi) = N_1 p(0, \pi)$.

replace N_2 by cV_1/M_2 with appropriate attention to units, we produce Eq. (6-32).

$$RT \ln \frac{p(\pi)}{p(0)} = RT \ln \frac{p(0, \pi)}{p(N_2, \pi)} = -RT \ln N_1 = RTN_2 = \frac{RTcV_1}{M_2} = V_1\pi \quad (6-36)$$

Thus it becomes clear that the osmotic pressure is large compared to the vapor pressure lowering because it corresponds to the change in total pressure that causes the lowering. Rearranging Eq. (6-33) and putting in finite changes in vapor pressure for a change in total pressure equal to the osmotic pressure, it is seen that the ratio is that of the volumes of equal weights of vapor and liquid, usually a factor of several hundredfold.

$$\frac{\pi}{\Delta p} = \frac{V_g}{V_l} \quad (6-37)$$

Equation (6-32) holds only at infinite dilution (or in a theta solvent, Sec. 7-3). At finite concentrations the osmotic pressure is best represented by an attenuated power series

$$\frac{\pi}{c} \frac{M}{RT} = 1 + A_2Mc + A_3M^2c^2 \quad (6-38)$$

where A_2 and A_3 are the *second* and *third virial coefficients*. Often, A_3 can be taken as equal to $(A_2/2)^2$, so that Eq. (6-38) can be rewritten:

$$\left(\frac{\pi}{c}\right)^{1/2} = \left(\frac{RT}{M}\right)^{1/2} \left(1 + \frac{A_2Mc}{2}\right) \quad (6-39)$$

Plots of $(\pi/c)^{1/2}$ versus concentration often are linear (Fig. 6-13) and allow extrapolation to infinite dilution. The second virial coefficient is obtained from such plots by dividing the slope by the intercept and by $M/2$.

Osmotic pressure probably is the most popular of the colligative methods. On the other hand, membrane preparation is tricky, equilibrium may be slow to be reached, and the effect observed, π , *decreases* as M increases. A commercially available automatic osmometer operates on the null-point principle; that is, solvent pressure is adjusted by a servomechanism until a sensor can detect no tendency for solvent to flow through the membrane in either direction (Fig. 6-14). Equilibrium can be reached in 5 or 10 min, so that the convenience of measurement approaches that of viscometry. With care, molecular weights of 10,000 to 500,000 can be measured with about 1% accuracy. Below 10,000, many polymers can penetrate the common membrane materials. When a low-molecular-weight polymer is placed in an osmometer, the rate of diffusion of the polymer through the membrane is discernible, since it results in a drift in the pressure necessary to maintain a null flow of solvent. Because the rate of diffusion decreases with increasing molecular size, the drift in osmotic pressure with time can be calibrated to yield the molecular weight of a specific polymer despite membrane penetration [16]. This is not an absolute method, of course.

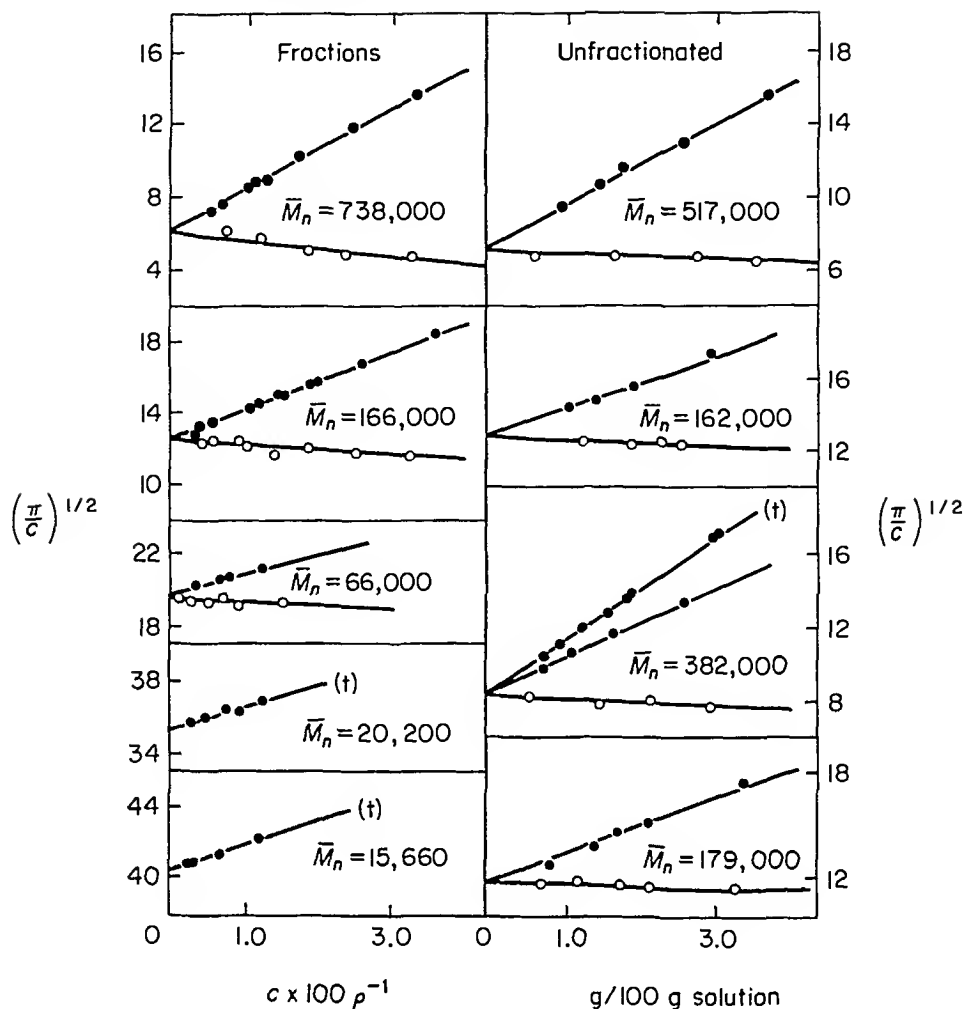


FIGURE 6-13

Osmotic pressures plotted according to Eq. (6-39) for poly(methyl methacrylate) in toluene [$\bullet(t)$], acetone ($\bullet$), or acetonitrile (o) [14].

For molecular weights less than about 20,000, another technique has been automated. In the so-called vapor pressure osmometer there is no membrane [17]. A drop of solution and a drop of pure solvent are placed on adjacent thermistors. The difference in solvent activity brings about a distillation of solvent from the solvent bead to the solution. The temperature change that results from the differential evaporation and condensation can be calibrated in terms of the number-average molecular weight of the solute. The method is rapid, although multiple concentrations and extrapolation to infinite dilution are still required.

6-7 WEIGHT-AVERAGE MOLECULAR WEIGHT METHODS

The scattering of light by small particles is a familiar phenomenon as, for example, the appearance of dust particles in a beam of sunlight. Similarly, if polymer molecules

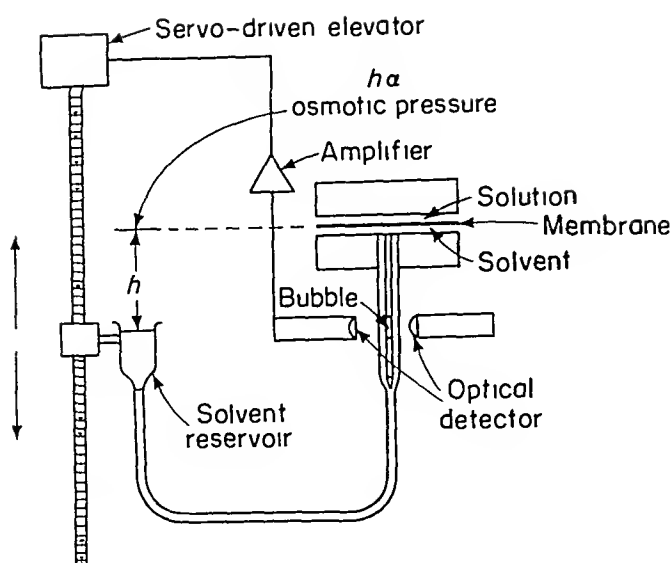


FIGURE 6-14
Automatic membrane osmometer [15].

are dissolved in a solvent, the light scattered by the polymer far exceeds that scattered by the solvent and is an absolute measure of molecular weight (Fig. 6-15). The Debye relationship is [18]

$$\frac{H'c}{\kappa} = \frac{1}{MP(\theta)} + 2A_2c \quad (6-40)$$

where H' is a lumped constant including geometric factors and also the change in refractive index with polymer concentration for the particular system being investigated. This latter relationship usually is established in a separate experiment using a differential refractometer. The intensity of light is measured at angle θ and concentration c . The second virial coefficient A_2 and a complex function of molecular shape $P(\theta)$ usually are derived from the data. The light intensity factor κ is derived from

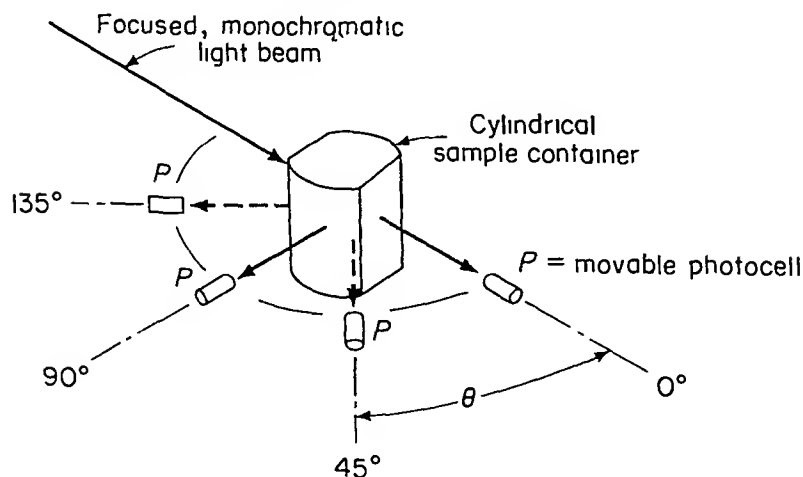


FIGURE 6-15
Photocell P senses light intensity I_θ at angle θ .

the raw galvanometer reading I_g when the photocell of Fig. 6-15 is at angle θ . One must compensate for geometry and the scattering by solvent, I_{gs} .

$$\kappa = \frac{(I_g - I_{gs}) \sin \theta}{1 + \cos^2 \theta} \quad (6-41)$$

Since it is known that $P(\theta) = 1$ at $\theta = 0$, it is customary to extrapolate to $\theta = 0$ as well as $c = 0$. This can be done by plotting $H'c/\kappa$ versus concentration at constant values of θ and then plotting the intercept $1/MP(\theta)$ versus $\sin^2(\theta/2)$ to give the intercept $1/M$. Both can be done simultaneously in a *Zimm plot* (Fig. 6-16), where a network results. As in osmotic pressure, measurements in a poor solvent give a low value for A_2 . Margerison and East [20] have worked out a complete example for polystyrene in benzene.

The extrapolation to $\theta = 0$ can be eliminated if scattering can be measured at forward angles of less than 2° from the incident beam. This becomes possible when the light source is a small, single transverse mode laser [21]. If the sample cell volume is made sufficiently small, laser beam light scattering can be used as the detector in column chromatography (GPC or HPLC). With the proper auxiliary apparatus and computational devices attached, the column effluent can be analyzed in terms of molecular weight directly without recourse to a separate calibration with molecular weight standards.

To see what kind of average molecular weight we measure by light scattering, we can examine the contributions made by individual species to the factor κ . For a monodisperse polymer i at $\theta = 0$:

$$\frac{H'c_i}{\kappa_i} = \frac{1}{M_i} \quad (6-42)$$

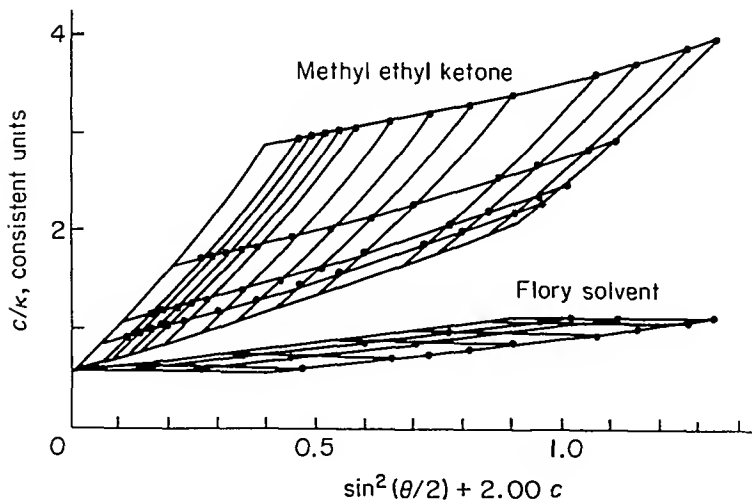


FIGURE 6-16

Zimm plots for scattering of light by poly(vinyl acetate) with $M_w = 3.0 \times 10^6$ in a good solvent, methyl ethyl ketone, and a poor one, methyl isopropyl ketone:*n*-heptane, 73.2:26.8. The ordinate has been adjusted to the same intercept with each solvent. (After [19].)

For a polydisperse polymer

$$\kappa = \sum \kappa_i = \sum H' c_i M_i \quad (6-43)$$

and

$$c = \sum c_i \quad (6-44)$$

The average molecular weight $\bar{M}$ is obtained from the overall scattering and concentration:

$$\bar{M} = \frac{\kappa}{H'c} = \frac{\sum H' c_i M_i}{H'c} = \frac{\sum c_i M_i}{c} = \sum w_i M_i \quad (6-45)$$

Thus it is seen that since c_i/c is the weight fraction of component i , w_i , the average molecular weight is M_w , the weight-average molecular weight.

A major practical problem in light scattering is the presence of dust particles or gelled polymer particles. A small concentration of these obscures the scattering by ordinary polymer particles and results in $\bar{M}_w = \infty$. Removal of dust by ultracentrifugation may be necessary, making this a rather expensive tool.

The ultracentrifuge itself can be used to measure a molecular weight distribution. Under exceptionally high gravitational fields, polymers will settle out of a solution just as macroscopic beads fall through a viscous liquid according to Stokes' law. In an ultracentrifuge [22] we balance the Brownian motion of the molecules against a centrifugal field and observe either the rate of settling or the equilibrium in the field. A cell holding the solution is placed in a head that rotates on air bearings up to 70,000 rpm. The concentration gradient across the cell is estimated using refractive index as a measure. Because extrapolation to $c = 0$ is still necessary and the difference in refractive index between solution and solvent must be large, the ultracentrifuge has been very successful only with certain classes of polymers, for example, proteins. It has not been as widely used as osmometry or light scattering as an absolute measure of molecular weight. A definite advantage of the ultracentrifuge is that the entire distribution is obtained, not just one lumped average molecular weight. Not only is M_w measured but M_n , M_z , etc., are measured directly without recourse to a mathematical model.

PROBLEMS

- 6-1. A polymer sample contains an equal number of moles N of species with degrees of polymerization $x = 1, 2, 3, 4, 5, 6, 7, 8, 9$, and 10 . What is x_n ? What is x_w ? ($N_1 = N_2 = N_3$, etc.)
- 6-2. Three samples of polymer are mixed without reaction. Calculate M_n and M_w for the mixture:

Sample	M_n	M_w	Weight in mixture, g
A	1.2×10^5	4.5×10^5	200
B	5.6×10^5	8.9×10^5	200
C	10.0×10^5	10.0×10^5	100

- 6-3. The molecular weight distribution for a certain polymer can be described as

$$w_x = \frac{kx}{10 + x^2} \quad x = 1, 2, \text{ and } 3 \text{ only}$$

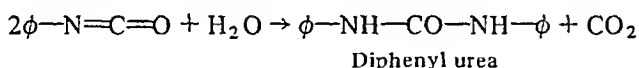
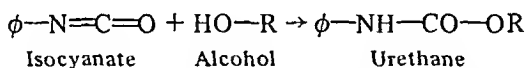
where w_x is the weight *fraction* of polymer with degree of polymerization x . What is the value of k ? What is the weight-average degree of polymerization, x_w ? What is x_n ?

- 6-4. A polymer sample has a molecular weight distribution described by

$$w_x = kx^2 \quad x = 1, 2, 3, \text{ and } 4 \text{ only}$$

where w_x is the weight fraction of polymer with degree of polymerization x . Calculate x_n and x_w .

- 6-5. One gram of polymer A ($x_n = 2000$, $x_w = 5000$) is mixed with 2 g of polymer B ($x_n = 6000$, $x_w = 10,000$). Calculate the degree of polymerization of the mixture that would be derived from osmotic pressure measurements at several concentrations.
- 6-6. The molecular weight of a polymer is 10,000 according to an osmotic pressure experiment in a theta solvent. What osmotic pressure (atm) do you expect to encounter at a concentration of 1.18 g/dl? A light-scattering experiment in a good solvent gives a molecular weight of 34,500. Why is there a difference in measured molecular weight? Would the difference be smaller or greater if the osmotic pressure were measured in a good solvent? ($R = 0.08206$ liter $\cdot$ atm/mol $\cdot$ K, and $T = 303$ K.)
- 6-7. Phenyl isocyanate (mol wt = 118) is expected to react quantitatively with primary alkyl hydroxyl groups to form urethanes and with water to form diphenyl urea.



Analysis of 100 g of a poly(ethylene oxide) with two hydroxyls per molecule results in 5.923 g of isocyanate being consumed with the evolution of 210 cm³ (at 1 atm, 25°C) of CO₂. Estimate x_n and the weight fraction of water in the polymer.

- 6-8. The following data are available for polymers A and B in the same solvent at 27°C:

Conc. c_A , g/dl	Osmotic pressure π_A , cm of solvent	Conc. c_B , g/dl	Osmotic pressure π_B , cm of solvent
0.320	0.70		
0.660	1.82	0.400	1.60
1.000	3.10	0.900	4.44
1.400	5.44	1.400	8.95
1.900	9.30	1.800	13.01

Solvent density = 0.85 g/cm^3 ; polymer density = 1.15 g/cm^3 .

(a) Plot $(\pi/c)^{1/2}$ versus c .

(b) Estimate M_n and the second virial coefficient for each polymer.

(c) Estimate M_n for a 25:75 mixture of A and B.

(d) If $M_w/M_n = 2.00$ for A and for B, what is M_w/M_n for the mixture of part c?

6-9 For a water-soluble polymer, what would be the upper limit on molecular weight measurable by freezing point depression?

6-10. Plot the Schulz distribution in cumulative form on logarithmic probability paper for $x_w/x_n = 2$ and 5. What parameter for the Wesslau model gives the best fit?

6-11. A polymer has a continuous cumulative distribution given by

$$W(x) = \ln(ea^2x^2 + 1) - \ln(a^2x^2 + 1)$$

where e is 2.7183 and a is an adjustable parameter. Derive expressions for the differential weight distribution and for x_w and x_n in terms of a . What is x_w/x_n ?

6-12. Compare the cumulative distribution of Prob. 6-11 with the Wesslau model on logarithmic probability paper using the product ax as the measure of molecular weight.

6-13. How could the model of Prob. 6-11 be modified to allow x_w/x_n to be an independent variable?

6-14. Show that the cumulative weight distribution for the Wesslau model, Eq. (6-25), is given by

$$W(x) = \int_0^x w_x dx = \frac{1 + \operatorname{erf}(Y/\beta)}{2}$$

where $Y = \ln(x/x_0)$ and erf is the normalized error function.

6-15. A polymer sample has a molecular weight distribution described by

$$w_x = k(x)^{1/2} \quad x = 1, 2, 3, 4, 5 \text{ only}$$

where w_x is the weight fraction of x -mer. Calculate $\bar{x}_n$, $\bar{x}_w$, and the polydispersity index.

6-16. Ten thousand elephants, while crossing the Alps in single file, are thrown into panic by the sudden blast of a pfschlngg. Each animal who panics entwines his trunk firmly about the tail of the preceding beast. In a quick but accurate survey, Hannibal finds that there now are as many elephants who are part of strung-together trios as there are singles (unattached elephants). How many of the ponderous pachyderms panicked?

6-17. Polymers A and B are monodisperse polystyrenes. Polymer A has a molecular weight three times that of B. Polymer C, on the other hand, is a polydisperse polystyrene for which M_w is 2.0×10^5 . Deduce the M_n for polymer C from the following measurements on a mixture of all three polymers: Mixture contains 25 g of A, 50 g of B, and 25 g of C. Light scattering gives a molecular weight of 112,500, while osmotic pressure gives a molecular weight of 60,000.

6-18. The molecular weight distributions of polymers A and B each can be represented by the "most probable" distribution. Also, $x_n > 100$ for each of them. When 200 g of A is mixed with 100 g of B, the polydispersity index $(x_w/x_n) = 4$ for the mixture. What is $(x_w)_A/(x_w)_B$?

6-19. In a polyesterification, 10-hydroxydecanoic acid is heated and water is removed.

Run A: 4.5 mol of water are removed from 5 mol of monomer.

Run B: 4.9 mol of water are removed from 5 mol of monomer.

(a) What are x_w and x_n for the polymer of Run B?

(b) If the two resultant polymers are combined without reaction, what is the x_w and x_n of the mixture?

6-20. A molecular weight distribution is given by

$$W = \log x - 1 \quad 10 < x < 100$$

$$W = 0 \quad x < 10$$

$$W = 1 \quad x > 100$$

where W is the cumulative weight fraction of polymer above degree of polymerization x . Calculate x_n and w_x .

6-21. A molecular weight distribution is represented by

$$\frac{dW}{dx} = Bxe^{-ax} \quad 0 < x < \infty$$

(a) Express B in terms of x_n .

(b) Determine the ratio of x_w to x_n .

(c) Plot $dW/d(x/x_n)$ versus $\log(x/x_n)$ for the range $0.1 < (x/x_n) < 10$.

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7

VISCOUS FLOW

7-1 DEFINITIONS

We have used the term “viscosity” up to now without a strict definition. In general, we know that polymer solutions flow more slowly through a tube than do solvents alone under the same pressure. Molten polymers flow much more slowly than do their solutions. Since many operations in production and fabrication involve flow in pipes, between rolls, and through slots and stirring in vessels, it is well for us to consider now some of the generalizations we can make regarding the effect of chemical and physical variables on flow properties.

Viscosity is a measure of the energy dissipated by a fluid in motion as it resists an applied shearing force. The dissipation is a form of friction and, in an adiabatic system, results in raising the temperature of the system. In laminar, unidirectional flow, the terms shear stress τ and rate of shear $\dot{\gamma}$ are used to indicate the applied force and the fluid's response. In the lamellar picture (Fig. 7-1), a certain force per unit of area f/A is required to maintain a constant-velocity gradient, in this case u/y . The quantities of interest are

$$\tau = \text{shear stress} = \frac{f}{A} \quad (7-1)$$

$$\dot{\gamma} = \text{rate of shear} = \frac{u}{y} \quad (7-2)$$

$$\eta = \text{shear viscosity} = \frac{\tau}{\dot{\gamma}} \quad (7-3)$$

For many liquids of lower molecular weight, Newton's law applies; i.e., the viscosity is a constant independent of the magnitude of τ or $\dot{\gamma}$. For many polymer melts and solu-

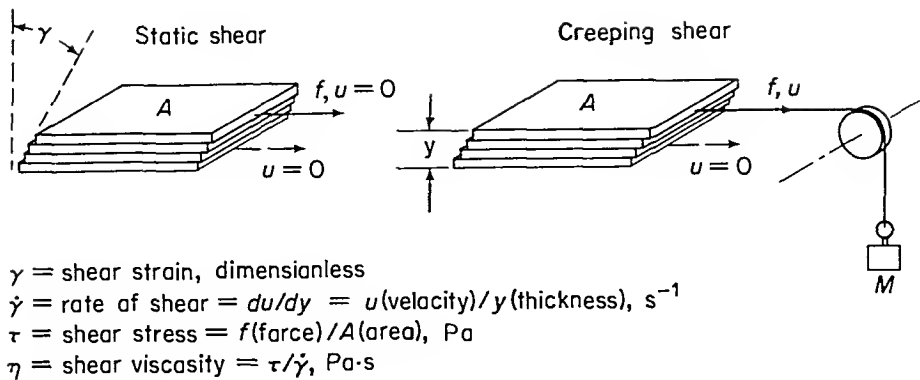


FIGURE 7-1
Viscosity in laminar, unidirectional flow (see Table 7-1).

tions, the shear stress and shear rate are not proportional over all ranges, so that the non-Newtonian viscosity as defined by Eq. (7-3) is not a constant. Another important quantity is the kinematic viscosity, the ratio of the absolute viscosity η to the density of the fluid ρ . Since units are often confusing in working out problems, an example is worked out in conjunction with Fig. 7-1 (Table 7-1). The rate of energy dissipation per unit volume $\dot{Q}$ for a flowing liquid is simply stated:

$$\dot{Q} = \eta \dot{\gamma}^2 = \tau \dot{\gamma} = \frac{\tau^2}{\eta} \tag{7-4}$$

If stress is in dynes per square centimeter and rate of shear in seconds, $\dot{Q}$ has the dimension of ergs per cubic centimeter per second. If stress is in pascals, then $\dot{Q}$ has the dimension of watts per cubic meter. In the example of Fig. 7-1, $\dot{Q}$ is 23.95 MW/m³ (or 5.72 cal/cm³·s). Remember that 1 W is 1 J/s or 0.2389 cal/s.

The viscous flow behavior of polymer melts and solutions is important as a relative measure of molecular weight. Also, since most forming operations involve flow, viscosity data often are gathered to predict processing characteristics. Some manufacturing methods with their typical associated shear rates are [1]:

- Compression molding $\dot{\gamma} = 1 \text{ to } 10 \text{ s}^{-1}$
Calendering $\dot{\gamma} = 10 \text{ to } 10^2 \text{ s}^{-1}$

TABLE 7-1
Viscosity in Laminar, Unidirectional Flow

	SI units	Metric units	Engineering units
Given: Mass M	0.454 kg	454 g	1.00 lb _m
Velocity u	0.305 m/s	30.5 cm/s	1.00 ft/s
Gap width y	$61 \times 10^{-6} \text{ m}$	$6.1 \times 10^{-3} \text{ cm}$	$2.00 \times 10^{-4} \text{ ft}$
Area A	$9.3 \times 10^{-4} \text{ m}^2$	9.3 cm^2	0.0100 ft^2
Constant g	9.81 m/s^2	981 cm/s^2	32.2 ft/s^2
Then: Stress τ	4.79 kPa	$4.79 \times 10^4 \text{ dyn/cm}^2$	$3.22 \times 10^3 \text{ lb}_m/\text{ft}\cdot\text{s}$
Shear rate $\dot{\gamma}$	$5.00 \times 10^3 \text{ s}^{-1}$	$5.00 \times 10^3 \text{ s}^{-1}$	$5.00 \times 10^3 \text{ s}^{-1}$
Viscosity η	0.958 Pa·s	9.58 poise	$0.644 \text{ lb}_m/\text{ft}\cdot\text{s}$

Extrusion	$\dot{\gamma} = 10^2 \text{ to } 10^3 \text{ s}^{-1}$
Injection molding	$\dot{\gamma} = 10^3 \text{ to } 10^4 \text{ s}^{-1}$

The most common instrument used for low-viscosity liquids is the capillary viscometer with liquid flowing under its own potential head (Fig. 7-2). The calibration equation for such a viscometer is [2]:

$$\frac{\eta}{\rho} = At - \frac{B}{t^2} \quad (7-5)$$

where B/t^2 is a correction factor for the kinetic energy losses at the entrance and exit to the capillary.

For flow when η is not constant but varies with τ or $\dot{\gamma}$, externally pressurized capillary and rotational viscometers are widely used (see Sec. 7-8).

7-2 POLYMER SHAPES IN SOLUTION [3, 4]

A treatment of amorphous polymers differs from that for low-molecular-weight materials because of the long covalent-bonded structure that must be accommodated. We shall treat here in outline some mathematical models for polymer shapes in solution that can be extended to polymer melts and cross-linked melts (rubbers).

A polymer molecule in solution is not a stationary piece of string, but instead is a constantly coiling and uncoiling chain whose conformation in space is ever changing. In a very dilute solution the individual molecules can be considered as acting independently. Each molecule can be pictured as a string of beads with a tendency to coil in upon itself to form a spherical cloud of chain segments having radial symmetry.

In order to see how the average size of the molecule's cloud changes with molecular weight, several approaches varying in their realism have been used. A simple

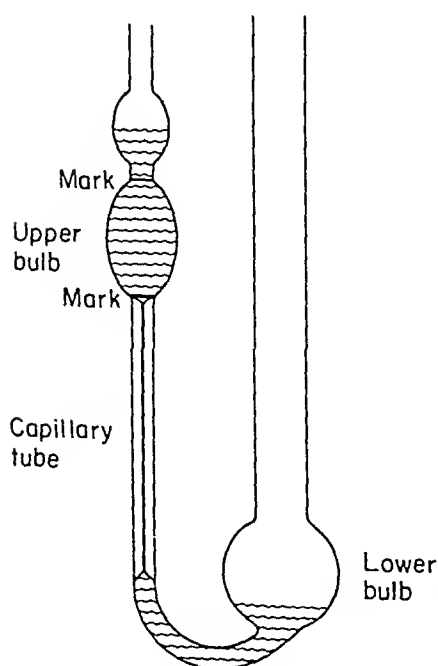


FIGURE 7-2

Ostwald viscometer. Time t is measured for fluid to flow out of upper bulb (between marks).

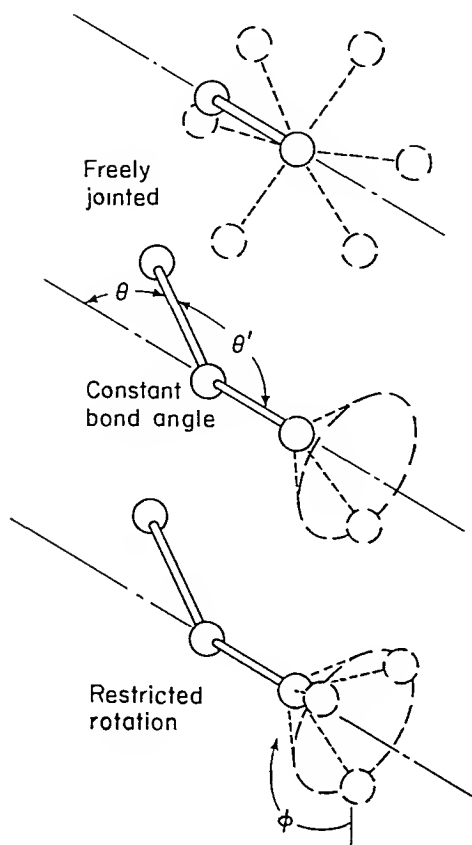


FIGURE 7-3
Polymer chain conformations.

model is that of the *freely jointed chain* (Fig. 7-3). If the chain has n links of length a , this is a “random flight problem.” Obviously, the average distance traveled $\bar{r}_0$ in flight of any number of links will be zero, since all starting directions are equally probable. However, the average square of the distance traveled $\bar{r}_0^2$ is not zero but increases linearly with the number of links:

$$\bar{r}_0^2 = na^2 \quad (7-6)$$

This is a rigid mathematical consequence of the assumed model and not an approximation. For example, polyethylene is composed of methylene groups, CH_2 , of molecular weight 14, separated by a bond distance of about 1.54 Å. Therefore, polyethylene of molecular weight 140,000 would have a root-mean-square end-to-end distance $(\bar{r}_0^2)^{1/2}$ of 15.4 nm. A more realistic approach includes the *constant* bond angle characteristic of any chemical combination. If θ' is the bond angle (109.5° for tetrahedral carbon) and $\theta = 180^\circ - \theta'$,

$$\bar{r}_0^2 = na^2 \frac{1 + \cos \theta}{1 - \cos \theta} \quad \text{or} \quad 2na^2 \text{ for carbon} \quad (7-7)$$

We are still assuming free rotation about each single bond. For the polyethylene of our previous example we would now get 21.8 nm.

However, we know that energy is required to rotate even one methylene group past another as in the paraffins. This is the phenomenon that has led to conformational analysis as a tool in the stereochemistry of organic compounds. Because there are energy barriers to rotation, the trans conformation is favored, although the probability of rotation increases with temperature. The gauche positions (Fig. 7-4) are more favorable than the cis position, or any other eclipsed conformation, but not as favorable as the trans position. In terms of the end-to-end distance, symmetrical, restricted rotation leads to

$$\overline{r_0^2} = na^2 \left(\frac{1 + \cos \theta}{1 - \cos \theta} \right) \left(\frac{1 + b}{1 - b} \right) \quad (7-8)$$

where b = average value of $\cos \phi$. Also, $b = 0$ for free rotation. Naturally, bulkier groups or planar groups tend to decrease rotation and give stiffer polymers.

Of course, r_0 is not the diameter of the polymer molecule "particle" or cloud. The rms distance of the elements of a chain from its center of gravity ($\overline{s^2}$)^{1/2} (radius of gyration) is related for linear polymers by

$$\overline{s^2} = \frac{\overline{r^2}}{6} \quad \text{and} \quad \overline{s_0^2} = \frac{\overline{r_0^2}}{6} \quad (7-9)$$

Branching of the polymer chain has the effect of decreasing r_g and s .

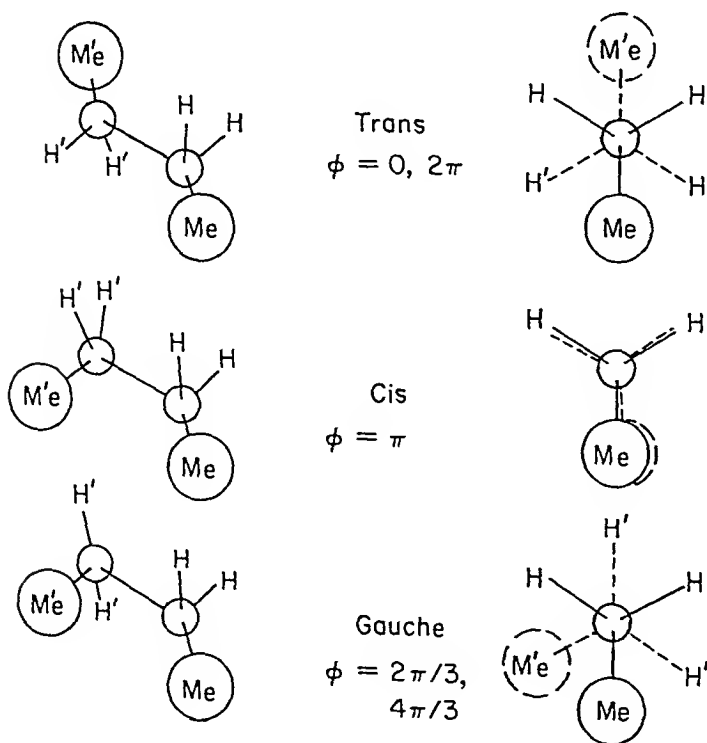
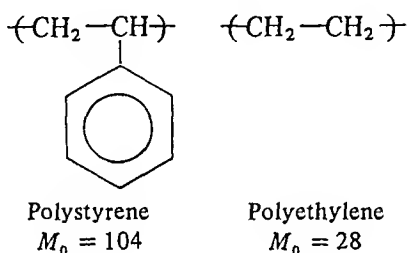


FIGURE 7-4

Conformations about a single bond for butane.

Other factors must be considered before experimental data can be interpreted theoretically. For example, random flight, even with constant bond angles and restricted rotation, does not keep more than one segment of the polymer chain from occupying the same volume at the same time. Thus a certain amount of volume is excluded, even under conditions such that no other forces act on the molecule.

In Table 7-2 some experimental values of molecular dimensions are compared with those calculated from Eq. (7-7) assuming free rotation about fixed bond angles. The experimental values for $\bar{r}_0^2/M$ in Table 7-2 were obtained from measurements (in poor solvents) of the intrinsic viscosity (Sec. 7-3). The steric factor σ includes the effects of restricted rotation and excluded volume. Often, substitution on a chain has two compensating effects on $(\bar{r}_0^2/M)^{1/2}$. The phenyl group in polystyrene compared to the hydrogen in polyethylene makes the molecule more compact. That is, the molecular weight per chain atom is about four



times as great. However, the bulky side group makes the chain stiffer, so that the polymer cannot coil up as readily, making the rms end-to-end distance per chain atom greater. The first effect outweighs the second, and it can be seen that polystyrene molecules occupy less volume per unit weight than polyethylene molecules of the same molecular weight at comparable temperatures. The ratio of volume is $(710/1030)^3$. On the other hand, the volume per chain atom (Table 7-2, second-last column) is greater for polystyrene. The ratio here is $(5.12/3.85)^3$.

A polymer molecule dissolved in a solvent will be more or less expanded depending on the degree to which solvent and polymer associate. If a polymer is in a "good" solvent, the segments of the polymer associate with the solvent molecules rather than with each other, expanding the total volume occupied by a single polymer cloud. We can define an expansion factor α by

$$\alpha = \left(\frac{\bar{r}^2}{\bar{r}_0^2} \right)^{1/2} \quad (7-10)$$

where $(\bar{r}^2)^{1/2}$ is the actual rms end-to-end distance and $(\bar{r}_0^2)^{1/2}$ is that when $\alpha = 1$ (unperturbed or unswollen dimension). Values of α have been determined experimentally and found to fit a theoretically derived relationship [6]

$$(\alpha^5 - \alpha^3) = C' M^{1/2} \left(1 - \frac{\theta_f}{T} \right) \quad (7-11)$$

where θ_f is the Flory temperature, C' is a constant for a given polymer-solvent combination, and M is the molecular weight. The Flory temperature θ_f is approximately

TABLE 7-2
Unperturbed Molecular Dimensions [5]

Polymer	Repeat unit	M/unit (n)	Temperature, °C	$K' \times 10^5$ $K' = [\eta]_0/M^{0.5}$	$(\overline{r_0^2}/M)^{0.5} \times 10^{11}$ cm exp.*	$(\overline{r_0^2}/M)^{0.5} \times 10^{11}$ cm calc.†	σ Steric factor*‡	$(\overline{r_0^2}/n)^{1/2}$ Å § exp.	$(\overline{r_0^2}/n)^{1/2}$ (Å) ¶ calc.
Polyisobutylene	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{CH}_3 \end{array}$	56 (2)	24 95	106 91	795 757	412 412	1.93 1.84	4.21 4.01	2.18 2.18
Polystyrene	$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{C}_6\text{H}_6 \end{array}$	104 (2)	70	75	710	302	2.35	5.12	2.18
Poly(methyl methacrylate)	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{C}=\text{O} \\ \\ \text{OCH}_3 \end{array}$	100 (2)	30	65	680	310	2.20	4.81	2.18
cis-Polyisoprene	$\begin{array}{c} \text{H} \qquad \text{CH}_2- \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{CH}_3 \quad \text{CH}_2- \end{array}$	68 (4)	0-60	119	830	485	1.71	3.42	2.00
trans-Polyisoprene	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_2- \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{CH}_2 \quad \text{H} \end{array}$	68 (4)	60	232	1030	703	1.46	4.25	2.90
Poly(dimethyl siloxane)	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{O}-\text{Si}- \\ \\ \text{CH}_3 \end{array}$	74 (2)	20	81	730	456	1.60	4.44	2.77
Polyethylene [6]	$-\text{CH}_2-\text{CH}_2-$	28 (2)	100	230	1030	582	1.77	3.85	2.18

* $(\overline{r_0^2}/M)^{0.5} = (K'/\phi)^{1/3}$, where $\phi = 2.1 \times 10^{21}$ dl/g·mol·cm³; 1 Å = 0.1 nm.
† From known angles and bond distances with free rotation.
‡ Ratio of exp. to calc. value of $(\overline{r_0^2})^{0.5}$.
§ From $(\overline{r_0^2}/M)$ exp.
¶ From $(\overline{r_0^2}/M)$ calc.

the temperature at which polymer of infinite molecular weight precipitates from the solvent. This is logical, because this is the point where polymer segments associate more with each other than they do with the solvent, reducing α to unity. Like the interaction parameter, θ_f is characteristic of a given polymer-solvent combination. Kurata and Stockmayer [7] list a number of examples of θ_f .

The experimental values of $(\bar{r}_0^2/M)^{1/2}$ in Table 7-2 were obtained in poor solvents at the point of precipitation. Under these conditions, the relationship between intrinsic viscosity and molecular weight, to be discussed in the next section, reduces to a form that gives $\bar{r}_0^2/M$ directly. Light scattering can also be used, but it is less convenient. The exact value of α depends also on the molecular weight. Some experimental values of α in a good solvent are shown in Table 7-3.

7-3 DILUTE SOLUTIONS AND INTRINSIC VISCOSITY

Manipulation of dilute solution viscosities yields an important parameter of a polymer in a given solvent, the intrinsic viscosity $[\eta]$. We can define $[\eta]$ as the ratio of specific viscosity η_{sp} to concentration c at infinite dilution.

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta - \eta_s}{c\eta_s} = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} \quad (7-12)$$

where η and η_s are viscosities of solution and solvent, respectively. It should be pointed out that only η and η_s have the dimensions of viscosity. Specific viscosity η_{sp} and relative viscosity $\eta_r = \eta/\eta_s$ are dimensionless. Intrinsic viscosity, reduced viscosity η_{sp}/c , and inherent viscosity $(\ln \eta_r)/c$ all have the dimensions of inverse concentrations. By convention, c is usually expressed as grams of polymer per deciliter (100 ml) of solution. The somewhat confusing nomenclature is summarized in Table 7-4. If either η_{sp}/c or $\ln \eta_r/c$ is plotted against c , a linear plot (Fig. 7-5) corresponding to the following equations may result:

Huggins [9]:

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c \quad (7-13)$$

TABLE 7-3
Dependence of α^3 on Molecular Weight [8]
Polyisobutylene in Cyclohexane, 30°C

Molecular weight $\times 10^{-3}$	Intrinsic viscosity, dl/g	$\alpha^3 = [\eta]/[\eta]_0$
9.5	0.145	1.39
50.2	0.47	1.96
558	2.48	3.10
2720	7.9	4.46

TABLE 7-4
Viscometric Terms

Symbol	Name	Common units
η	Solution viscosity	Poise or Pa·s
η_s	Solvent viscosity	Poise or Pa·s
$\eta_r = \eta/\eta_s$	Relative viscosity	Dimensionless
$\eta_{sp} = \eta_r - 1$	Specific viscosity	Dimensionless
$(\ln \eta_r)/c$	Inherent viscosity	dl/g
η_{sp}/c	Reduced viscosity	dl/g

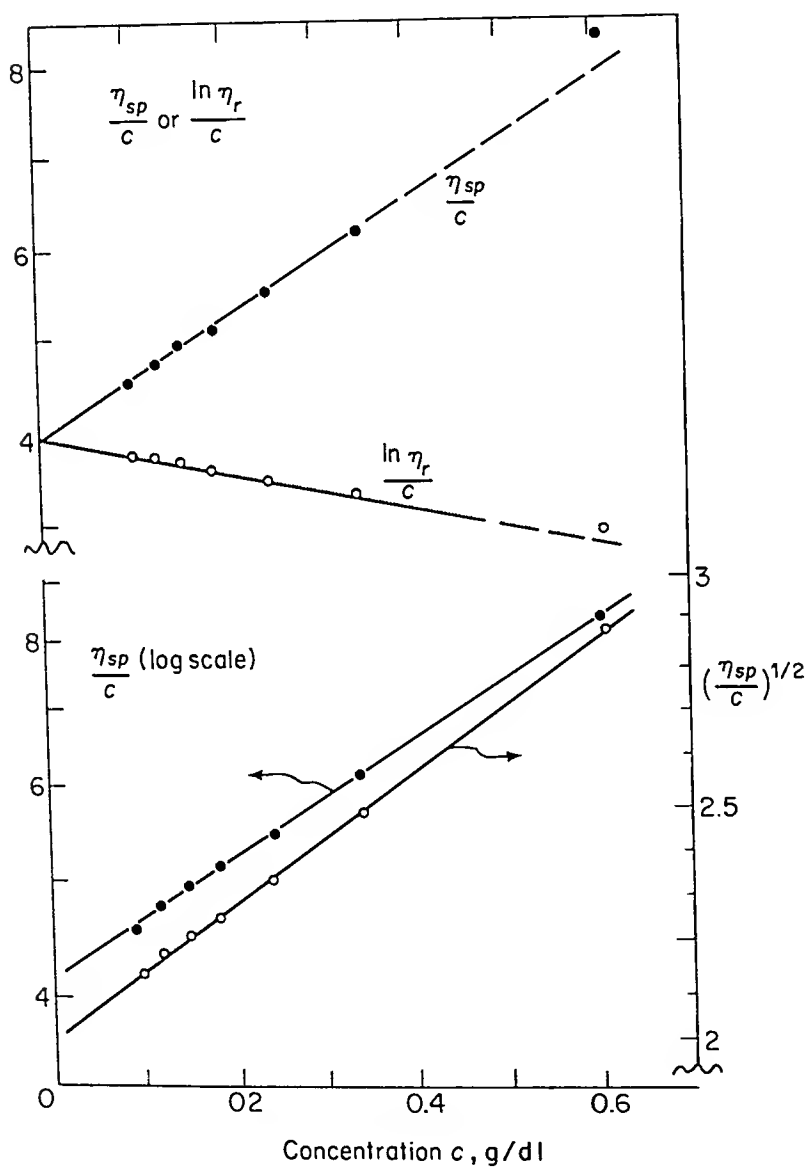


FIGURE 7-5
Correlations for viscosity of dilute solutions.

Kraemer [10]:

$$\frac{\ln \eta_r}{c} = [\eta] - k'' [\eta]^2 c \quad (7-14)$$

For many polymers in good solvents

$$k' = 0.4 \pm 0.1 \quad \text{and} \quad k'' = 0.05 \pm 0.05$$

The equations cited are applicable only in dilute solutions where η_r is less than about 2. In analogy to the treatment of osmotic data [Eq. (6-43)], we can linearize data to higher concentrations if we postulate an equation of the form [11]:

$$\left(\frac{\eta_{sp}}{c} \right)^{1/2} = [\eta]^{1/2} + \frac{k'''}{2} [\eta]^{3/2} c \quad (7-15)$$

This equation and another mentioned later [Eq. (7-22)] are compared with the Huggins and Kraemer equations in Fig. 7-5 and Table 7-5 for a set of experimental data.

Staudinger [12] proposed on empirical grounds that $[\eta]$ was proportional to molecular weight for a given polymer-solvent combination. The more general Mark-Houwink relationship [13] with two constants, K' and a , is

$$[\eta] = K' M^a \quad (7-16)$$

Typical values of K' and a are summarized in Table 7-6.

The practical importance of intrinsic viscosity cannot be overstated. It is the most common measure of molecular weight for high polymers. The average molecular weight measured by viscosity M_v lies between M_n and M_w , which are measured by osmotic pressure and light scattering, respectively (see Secs. 6-5 and 6-6). The experimental results give

$$[\eta] = \sum_{x=1}^{\infty} w(x) [\eta](x) \quad (7-17)$$

where $[\eta]$ is the intrinsic viscosity of the whole polymer made up of fractions weighing $w(x)$ each and possessing an intrinsic viscosity $[\eta](x)$ each. Combination of Eq. (7-16) with Eq. (7-17) yields

$$M_v = [\sum w(x) M(x)^a]^{1/a} \quad (7-18)$$

TABLE 7-5
Parameters for Fig. 7-5

Equation	$[\eta]$	Slope factor
7-13	3.95	$k' = 0.41$
7-14	3.97	$k'' = 0.12$
7-15	3.99	$k''' = 0.36$
7-22b	4.14	$K'' = 0.12$

TABLE 7-6
Parameters for the Mark-Houwink Equation [7]

Polymer	Solvent	Temperature, °C	$K' \times 10^5$	a
Cellulose triacetate	Acetone	25	8.97	0.90
SBR rubber	Benzene	25	54	0.66
Natural rubber	Benzene	30	18.5	0.74
	<i>n</i> -Propyl ketone	14.5	119	0.50
Polyacrylamide	Water	30	68	0.66
Polyacrylonitrile	Dimethyl formamide	25	23.3	0.75
Poly(dimethylsiloxane)	Toluene	20	20.0	0.66
Polyethylene	Decalin	135	62	0.70
Polyisobutylene	Benzene	24	107	0.50
	Benzene	40	43	0.60
	Cyclohexane	30	27.6	0.69
Poly(methyl methacrylate)	Toluene	25	7.1	0.73
Polystyrene				
Atactic	Toluene	30	11.0	0.725
Isotactic	Toluene	30	10.6	0.725
Poly(vinyl acetate)	Benzene	30	22	0.65
	Ethyl <i>n</i> -butyl ketone	29	92.9	0.50
Poly(vinyl chloride)	Tetrahydrofuran	20	3.63	0.92

$$\text{or } x_v = [\sum w(x)x^a]^{1/a} \quad (7-19)$$

For the example of Chap. 6 (Table 6-2) the student can verify that x_v is equal to 2.74 or 2.83 when the exponent of Eq. (7-19) is equal to 0.5 or 0.67, respectively. In either case, it should be noted, M_v is much closer to M_w than to M_n . If the exponent $a = 1$, then $M_v \equiv M_w$.

In comparison to light scattering, viscosity measurements involve far less time and equipment. In comparison to osmotic pressure, viscosity has the advantage that the observable quantity increases as molecular weight increases (Fig. 7-6). Of course, some absolute method such as light scattering or osmotic pressure measured on fractions where x_w/x_n is small (for example, $x_w/x_n < 1.2$) must be used to "calibrate" Eq. (7-16) for a given polymer and solvent.

The connection between Eq. (7-16) and Eqs. (7-6), (7-10), and (7-11) is made by assuming the polymer molecule to be a random, spherical coil of beads when the molecular weight is high enough. At infinite dilution each molecule acts separately from other polymer molecules. In a shear field (velocity gradient du/dy , s^{-1} , or $\dot{\gamma}$), the sphere rotates with a frequency ω rad/s, where $\omega = \dot{\gamma}/2$.

The work necessary to rotate this complex sphere, part beads, part perturbed solvent, part immobilized solvent, is measured by the viscosity. Several theories [14] lead to the idea that

$$[\eta] = \Phi \frac{(\bar{r}^2)^{3/2}}{M} \quad (7-20)$$

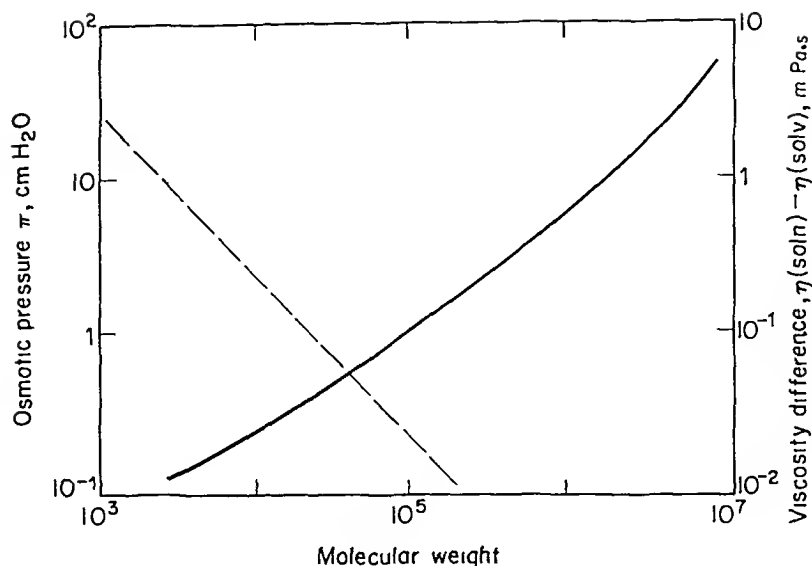


FIGURE 7-6
Effect of molecular weight on observable quantities.

where Φ is a universal constant. When $\bar{r}^2$ (cm^2) and M (g/mol) are measured by light-scattering and $[\eta]$ (dl/g) is measured under the same conditions, Φ can be evaluated. A number of such measurements gives $\Phi = 2.1 \pm 0.2 \times 10^{21}$ ($\text{dl/mol} \cdot \text{cm}^3$). Since $(\bar{r}_0^2/M)^{1/2}$ is nearly constant (Table 7-2), it is convenient to combine Eqs. (7-10) and (7-20) to give

$$[\eta] = \Phi \left(\frac{\bar{r}_0^2}{M} \right)^{3/2} M^{1/2} \alpha^3 \quad (7-21)$$

This states that the intrinsic viscosity should vary with $M^{1/2}$ in any solvent at the Flory point ($T = \theta_f$) or that $a = 0.5$ in Eq. (7-16). At any higher temperature, α varies with M according to Eq. (7-11). If $\alpha \gg 1$, then $\alpha^5 \gg \alpha^3$ and $\alpha^3 \sim M^{0.3}$. In practice, Eq. (7-16) expresses Eq. (7-21) combined with Eq. (7-11) to a good approximation when $0.5 < a < 0.8$.

The value of α obviously characterizes the "goodness" of a solvent. Since Φ and $(\bar{r}_0^2/M)^{1/2}$ are relatively constant, the variation of $[\eta]$ with solvent for a polymer of given molecular weight is a good measure of the solvating ability of the solvent and of the volume of solution occupied per unit weight of polymer at high dilution.

Because $\bar{r}_0^2/M$ is known to be relatively insensitive to temperature or solvent character, the ratio of $[\eta]$ to $[\eta]_\theta$ (in a solvent at the Flory temperature) gives a good idea of α^3 no matter what solvent was used to measure $[\eta]_\theta$. Thus, taking values of K' and a from Table 7-6, we get for polyisobutylene in cyclohexane at 30° :

$$\alpha^3 = \frac{[\eta]}{[\eta]_\theta} = \frac{K' M^a(\text{cyclohexane}, 30^\circ\text{C})}{K' M^a(\text{benzene}, 24^\circ\text{C})} = 0.258 M^{0.19}$$

So for $M = 10^6$, $\alpha^3 = 3.56$, that is, the individual polymer molecules occupy almost four times the volume in cyclohexane than they do in any theta (Flory) solvent.

It was mentioned in Sec. 2-5 that polymers in contact with solvents of like solubility parameter δ should show the greatest solvation effects, i.e., swelling of networks or viscosity of solutions. Now we can identify this solvating ability with α , the expansion factor in Eq. (7-10).

7-4 EFFECT OF CONCENTRATION AND MOLECULAR WEIGHT

Equations (7-13), (7-14), and (7-15) hold only in dilute solution. Many other equations have been proposed to express the variation of viscosity with concentration even at moderate concentrations. One empirical approach is that of Lyons and Tobolsky [15], who proposed

$$\frac{\eta_{sp}}{c[\eta]} = \exp \left(\frac{k'_L [\eta] c}{1 - b} \right) \quad (7-22a)$$

In the limit of very dilute solutions, $k'_L/(1 - b)$ should be the same as k' in the Huggins equation [Eq. (7-13)]. Under some conditions this one equation can represent the low shear (Newtonian) viscosity of a single polymer from dilute solution to the solvent-free melt [16]. The constant b can be positive or negative. The equation resembles a theoretical relationship derived by Fujita and Kishimoto based on fractional free volume contributions by polymer and solvent [17, 18]. A simpler form, in which b is zero, was used by Martin some years earlier:

$$\log \frac{\eta_{sp}}{c} = \log [\eta] + K'' [\eta] c \quad (7-22b)$$

This equation (see Fig. 7-5) has been very popular, because it involves only two fitted constants, yet can correlate data to high concentrations. It, together with some other empirical equations, is treated more extensively by Ott and Spurlin [19]. As one approaches the pure molten polymer, that is, $c > 50$, the particular solvent used seems to have little bearing on the viscosity, and $\eta(\text{solution}) = \eta(\text{polymer})v_2$, where v_2 is the volume fraction of polymer [20].

Combination of Eq. (7-16) with (7-13), (7-14), (7-15), or (7-22b) gives the effect of molecular weight on η for solutions. For polymer melts several approaches are suggested. Log-log plots of η versus M often can be resolved into two straight lines. Typical behavior of melts over a large range of molecular weight is shown in Fig. 7-7. The upper section in Fig. 7-7 has a slope of 3.5 ± 0.5 , and the lower section has a slope closer to 1 or 2. For each section we can write

$$\log \eta = A \log M_w + B \quad (7-23)$$

The break in the curve is thought to represent the molecular weight at which polymer entanglements become serious enough to contribute heavily to the viscosity. Single

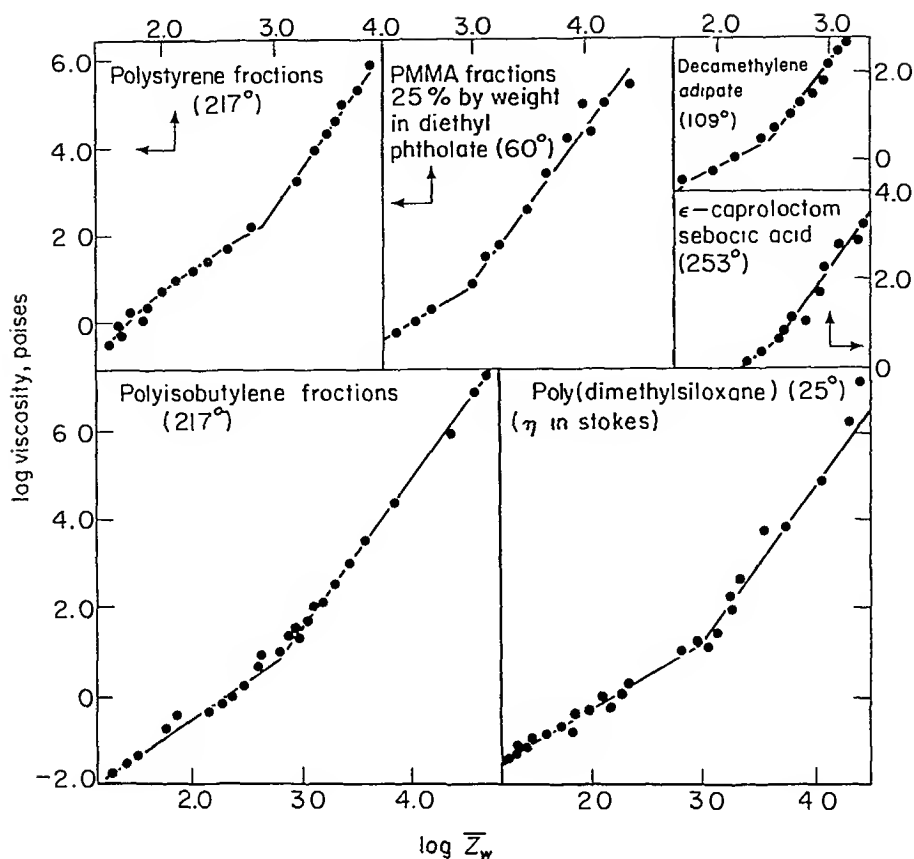


FIGURE 7-7

Logarithmic plots of viscosity η vs. weight-average number of chain atoms Z_w for six polymers [20]; 1 poise = 0.1 Pa·s.

polymer molecules no longer diffuse separately, but drag along neighbors. An analogy would be the removal of a piece of string from a pile of strings. As the average length of strings increases, the difficulty of removing the string increases. Some values of this “entanglement molecular weight” are given in Table 7-7. Over a limited range of molecular weight, another relationship has some usefulness [20]:

$$\log \eta = A + BM^{1/2} \quad (7-24)$$

7-5 EFFECT OF TEMPERATURE AND PRESSURE

Viscous flow can be pictured as taking place by the movement of molecules or segments of molecules in jumps from one place in a lattice to a vacant hole. The total “hole concentration” can be regarded as space free of polymer, or “free volume.” Doolittle proposed [21] that the viscosity should vary with the free V_f in the following way:

$$\log \eta = A + \frac{BV_0}{V_f} \quad (7-25)$$

where A and B are constants, V_f is the *free volume* equal to $V - V_0$, V is the specific volume (per unit weight), and V_0 is the specific volume extrapolated from the melt to 0 K without change of phase. The fractional free volume $f' = V_f/V$ is expected to vary with temperature as follows:

$$f' - f'_g = \alpha \Delta T \quad (7-26)$$

where α is the difference between the expansion coefficients for melt and glass, $\Delta T = T - T_g$, and f'_g is the fractional free volume at T_g . For many polymers α is about $4.8 \times 10^{-4} \text{ K}^{-1}$. Also, Williams, Landel, and Ferry [22] found empirically that

$$\log \left(\frac{\eta}{\eta_g} \right) = \frac{-17.44(T - T_g)}{51.6 + (T - T_g)} = \frac{-17.44 \Delta T}{51.6 + \Delta T} \quad (7-27)$$

TABLE 7-7

Applicability of the Empirical Law $\log \eta = 3.4 \log Z_w + K$ to Long Polymer Chains [20]

Polymer solvent pair	Range of applicability				
	[Polymer], wt fraction	$v_2 Z_c$ at break*	Highest Z studied	Temperature range studied, °C	Polymers and mol wt detm'n†
Linear nonpolar polymers					
Polyisobutylene	1.0	610	53,000	-9 to 217	$f:(\eta)$
Polyisobutylene-xylene	0.05 to 0.20	~1400	140,000	25	$W \& f:(\eta)$
Polyisobutylene-decalin	0.05 to 0.20	—	140,000	25	$W \& f:(\eta)$
Polystyrene	1.0	730	7,300	130 to 217	$f:(\eta)$
Polystyrene-diethyl benzene	0.14 to 0.44	~1000	22,500	30 to 100	$f:(\eta)$
Poly(dimethylsiloxane)	1.0	~950	34,000	25	$W:\pi, \text{L.S.}$
Linear polar polymers					
Poly(methyl methacrylate)- diethyl phthalate	0.25	208	24,000	60	$f:(\eta)$
Decamethylene sebacate	1.0	290	960	80 to 200	$W:E$
Decamethylene adipate	1.0	280	1,320	80 to 200	$W:E$
Decamethylene succinate	1.0	290	990	80 to 200	$W:E$
Diethylene adipate	1.0	290	1,190	0 to 200	$W:E$
ω -Hydroxy undecanoate	1.0	<326	1,443	90	$W:E$
Effect of branching					
Poly(ϵ -caprolactam):					
Linear	1.0	324	2,300	253	$W:E$
Tetrachain	1.0	390	1,560	253	$W:E$
Octachain	1.0	550	2,000	253	$W:E$

* Z_c is the lowest chain length for which equation is valid for the solution wherein v_2 is the volume fraction of polymer.

† f = fraction, W = whole polymer. Chain lengths determined from η = intrinsic viscosity, π = osmotic pressure, L.S. = light scattering data, E = end group analysis.

where η_g is the viscosity at T_g . We can combine Eqs. (7-25), (7-26), and (7-27) if we replace V_0 in Eq. (7-25) by V . This is not too great a change, since, unlike V_f , V does not change rapidly with temperature. First we write Eq. (7-25) as the difference of two conditions to eliminate the constant A .

$$\log \frac{\eta}{\eta_g} = -\frac{B(f' - f'_g)}{f'_g f'} \quad (7-28)$$

Equation (7-26) is used to eliminate f' :

$$\log \frac{\eta}{\eta_g} = \frac{(-B\alpha \Delta T)}{f'_g(f'_g + \alpha \Delta T)} = \frac{(-B/f'_g) \Delta T}{(f'_g/\alpha) + \Delta T} \quad (7-29)$$

Identification of Eq. (7-29) with Eq. (7-27) shows that $f'_g = 51.6\alpha$ or 0.025. The conclusion is drawn that the glass transition occurs for all materials (polymers and inorganic glasses, low-molecular-weight compounds) at a temperature where the fractional free volume is 2.5% of the total, since the empirical relationships used have been found to apply for all these materials.

When $T - T_g > 100^\circ\text{C}$, Eq. (7-27) does not work as well as the more general one [20]:

$$\log \frac{\eta}{\eta_R} = B' \left(\frac{1}{T^a} - \frac{1}{T_R^a} \right) \exp \left(-\frac{\beta}{M} \right) \quad (7-30)$$

where η_R is the viscosity at a reference temperature T_R for molecular weight M and a usually is an integer, while B' and β are fitted constants. Some typical results are seen in Fig. 7-8.

One would expect the compression of a melt to decrease the free volume and consequently increase the viscosity. It can be seen that the viscosity of highly compressible polystyrene is affected more by pressure than that of the less compressible polyethylene (Fig. 7-9). It will be remembered (Sec. 7-2, Table 7-2) that polystyrene had a higher value of r_0^2/n than polyethylene. Because increasing pressure will increase the glass transition temperature, it is possible to use Eq. (7-27) with a pressure-dependent T_g to correlate viscosity if one knows the form of the dependence [24, 25]. For several polymers, $d(T_g)/dP$ is reported to be in the range of 0.16 to 0.43°C/MPa. Polystyrene, for example, has a value of 0.3°C/MPa [24]. It is harder to generalize about the temperature and pressure dependence of polymer solutions. Also, logarithmic plots of viscosity vs. concentration are not linear, especially in concentrated solutions (Fig. 7-10).

7-6 MODELS FOR NON-NEWTONIAN FLOW

It has been assumed until now that the viscosity is a constant for any polymer with a given molecular weight, solvent, concentration, temperature, and pressure. Two more variables are the rate at which deformation takes place and the length of time at a given rate of shear. For even if we hold the rate of deformation constant, the viscosity

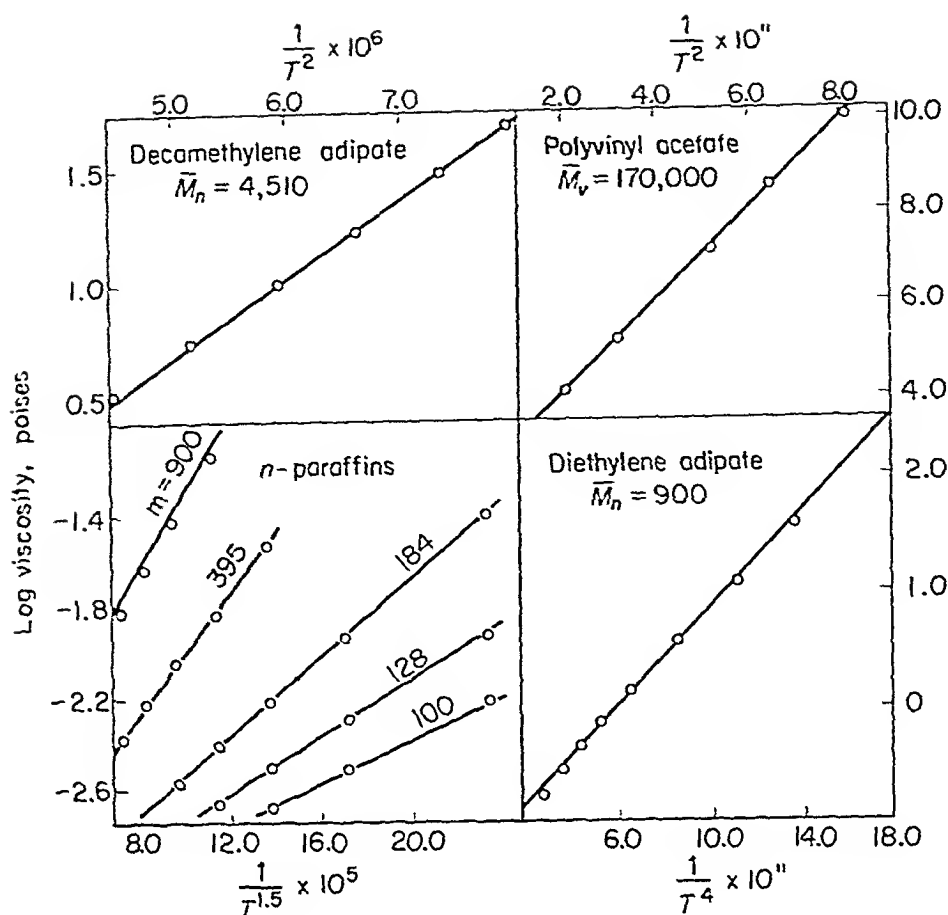


FIGURE 7-8

Viscosity-temperature curves according to Eq. (7-30) [20].

may increase or decrease with time. If the effect is temporary and viscosity goes back to its original value (after the system has relaxed long enough with no deforming forces imposed), we call the behavior *rheopexy* (viscosity increases with time of deformation) or *thixotropy* (viscosity decreases with time of deformation) (Fig. 7-11). One expects this behavior when viscosity is partially due to intermolecular structures that take some time to be established or destroyed. Ionic polymers in water tend to be thixotropic, because the polymers probably aggregate when relaxed but disperse and act individually when sheared.

The variation of viscosity with rate of deformation can be shown by a combination of any two variables τ , $\dot{\gamma}$, or η , since η can be defined as a variable by Eq. (7-3). Behavior can be dilatant (viscosity increases with $\dot{\gamma}$ or τ) or pseudoplastic (viscosity decreases with $\dot{\gamma}$ or τ) (Fig. 7-12). Most examples of dilatant behavior are particulate dispersion such as latexes, slurries, and concentrated suspensions. In slurries and concentrated suspensions there may be almost no flow, $\dot{\gamma} = 0$, until τ reaches some "yield value" (Fig. 7-12). Ordinary toothpaste approaches this "Bingham plastic" behavior.

The typical behavior of polymer solutions and melts is pseudoplastic. The development of a single mathematical model to express the behavior of all such materials has not been successful. One of the simplest approaches [26] is to approximate sections of $\log \tau$ - $\log \dot{\gamma}$ plots by straight lines—the "power-law" model (Fig. 7-12):

$$\tau = K\dot{\gamma}^n \quad (7-31)$$

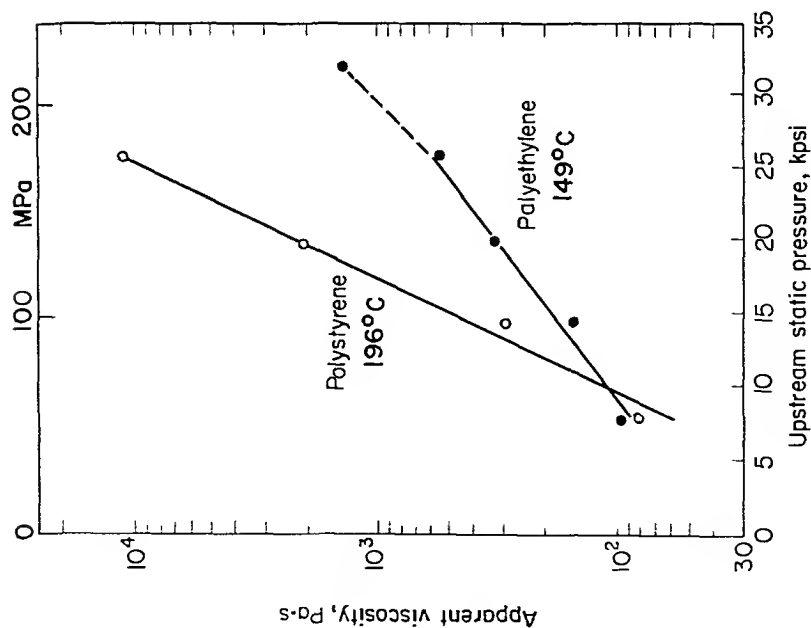


FIGURE 7-9
Corrected apparent viscosity vs. upstream static pressure for polyethylene and polystyrene [23].

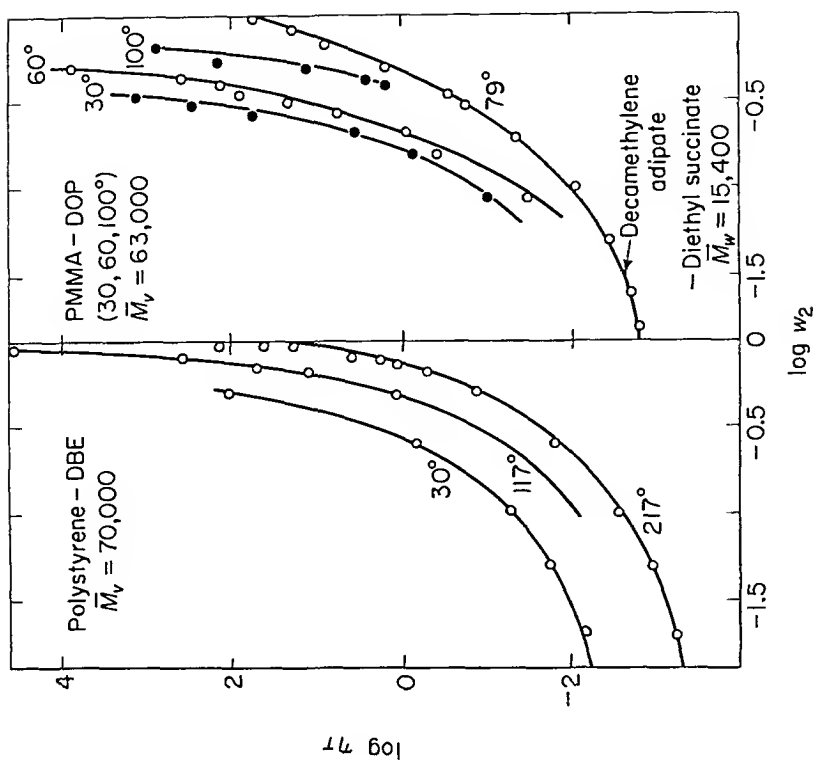


FIGURE 7-10
Dependence of viscosity (Pa-s) on the weight fraction w_2 of polymer in solution at various temperatures. DBE is dibenzyl ether, PMMA-DEP is poly(methyl methacrylate) in diethyl phthalate [20].

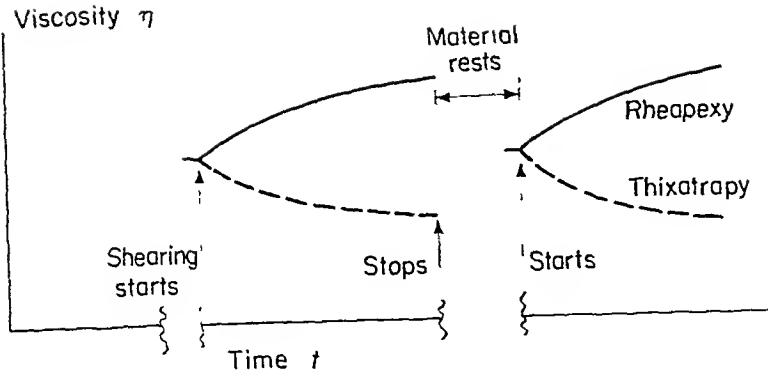


FIGURE 7-11

Schematic behavior of time-dependent viscosity, which increases (rheopexic behavior) or decreases (thixotropic behavior) with time during shearing at a steady rate. Resting the material allows the pattern to be observed again.

It can be seen from flow curves for a polymer melt (Fig. 7-13) that Eq. (7-31) would serve well over several decades of shear rate but would fail as the melt approaches Newtonian behavior. Even in polymer solutions (Figs. 7-14 and 7-15) the power law is adequate over a decade or so in shear rate. In the case of the solutions, the lines are drawn according to a different mathematical model [27].

The power-law model is attractive in its simplicity. However, as stress or rate of shear becomes small, the viscosities of almost all polymer melts, solutions, latexes, and some other dispersions appear to approach a constant value η_0 , the zero-shear-rate viscosity (Fig. 7-12). In the case of the power-law, as τ or $\dot{\gamma}$ goes to zero, viscosity becomes infinite when n is less than 1. The Ellis model is a mathematical combination of Newtonian behavior at low values of τ , and power-law behavior at high values of τ [29].

$$\frac{\eta_0}{\eta} - 1 = k\tau^a \quad (\text{"Ellis"}) \quad (7-32)$$

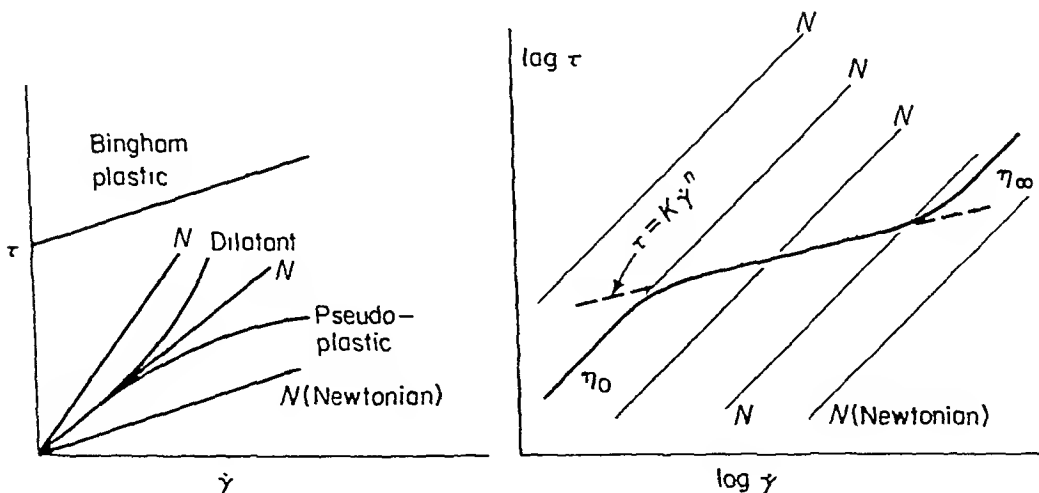


FIGURE 7-12

Stress vs. rate of shear on arithmetic and logarithmic coordinates for Newtonian and non-Newtonian fluids.

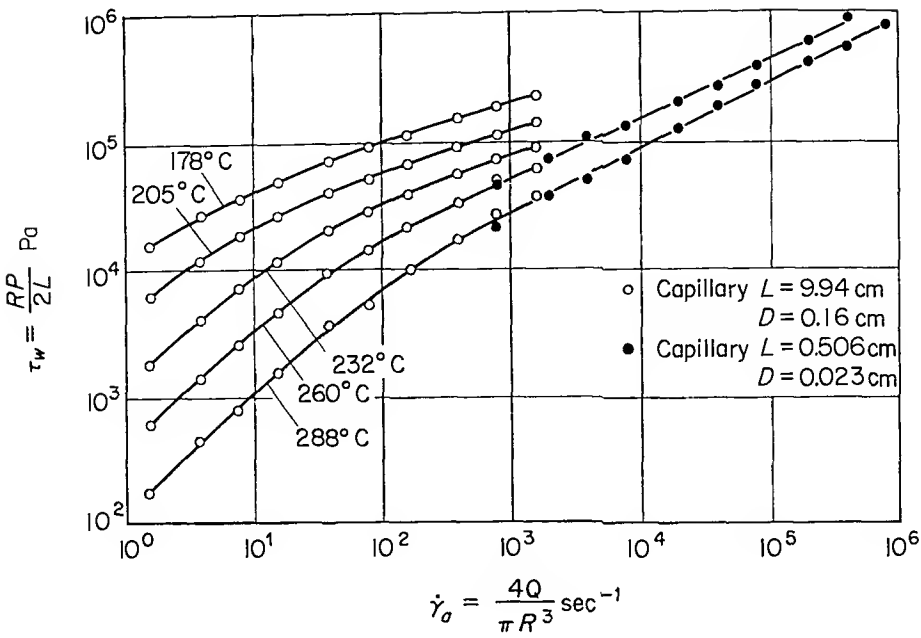


FIGURE 7-13
Flow curves for a commercial sample of polystyrene at various temperatures obtained in a ram-extrusion type of capillary viscometer [1].

or $\eta_0 \dot{\gamma} = \tau + k\tau^{1+a}$ (7-33)

For polymer solutions, there is evidence that the viscosity approaches a constant value less than η_0 but greater than that of the solvent as the rate of shear becomes very large. In most two-parameter models, this viscosity at infinite shear rate η_∞ is zero (Fig. 7-13).

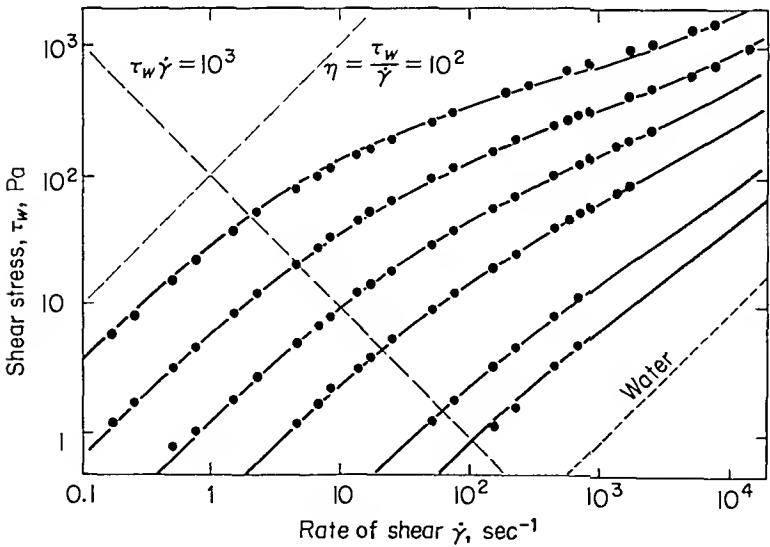


FIGURE 7-14
Flow curves for six concentrations of polyacrylamide. Lines are drawn according to a model [27].

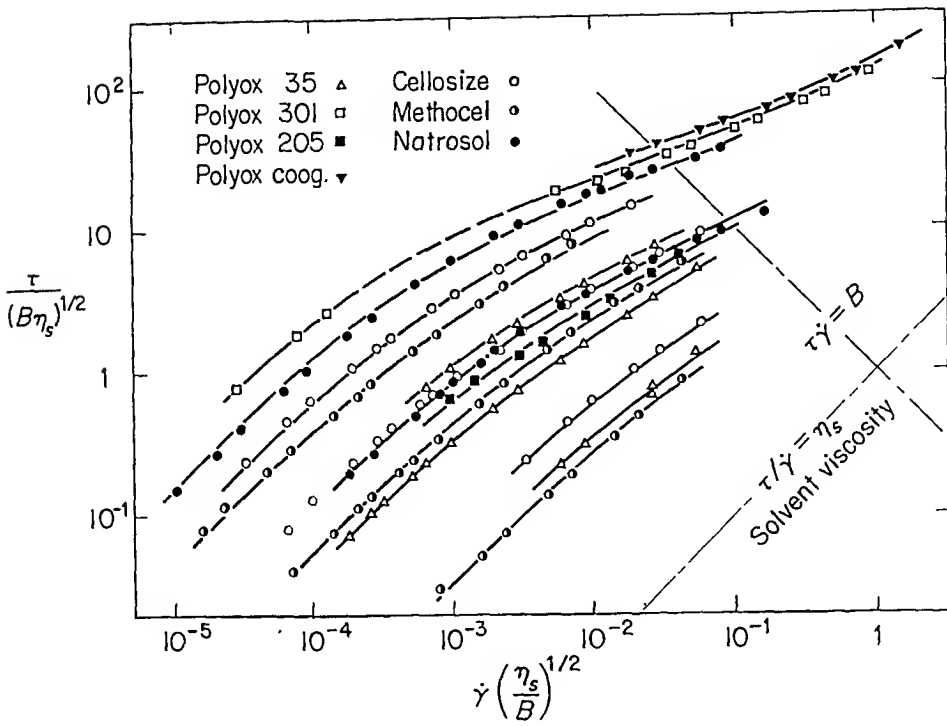


FIGURE 7-15

Flow curves for polymer solutions in water with lines drawn according to a model [28].

By going to three or more parameters, there is a better possibility of including η_∞ as a finite number. The Ellis model is an exception, since η_∞ must be zero. However, the Williamson [30], Krieger-Dougherty [31], Eyring-Powell [32], and Reiner-Philippoff [33] models can be written with finite values for η_0 and η_∞ .

There is another class of equations that derives the dependence of viscosity on $\dot{\gamma}$ or τ from a different kind of experiment. Pao [34] has developed one which can be put in the form

$$\eta = \sum_1^N \frac{\mu_i \phi_i}{1 + \phi_i^2 \dot{\gamma}^2} + \frac{\sum_1^N [\mu_i \phi_i^2 / (1 + \phi_i^2 \dot{\gamma}^2)]^2}{\sum_1^N [\mu_i \phi_i / (1 + \phi_i^2 \dot{\gamma}^2)]} \quad (34)$$

where μ_i is a modulus and ϕ_i is a relaxation time. This equation demands a knowledge of the distribution of relaxation times (from 1 to N) obtained perhaps from creep recovery or stress relaxation experiments. Even using a simple Rouse distribution [35] calls for the specification of a maximum relaxation time together with a modulus. The modulus can be eliminated by introducing η_0 . In the Rouse model μ_i is a constant and

$$\phi_i = \frac{\phi_0}{p^2} \quad p = 1, 2, 3, \dots, N \quad (7-35)$$

where N is a function of molecular weight. Pao's equation can thus be converted to

$$\frac{\eta}{\eta_0} = \frac{\Sigma (1/p^2) \Sigma p^2 / (p^4 + \phi^2 \dot{\gamma}^2)}{[\Sigma p^2 / (p^4 + \phi^2 \dot{\gamma}^2)]^2 + \phi^2 \dot{\gamma}^2 [\Sigma 1 / (p^4 + \phi^2 \dot{\gamma}^2)]^2} \quad (7-36)$$

(All summations from 1 to ∞ , $\phi = \phi_0$)

In this form it is an equation with two adjustable parameters, η_0 and ϕ_0 , provided N is very large, i.e., infinite.

Often only a narrow range of shear rates or stresses is important. In molecular weight characterization, η_0 is used. In capillary flow at high shear rates, the shear stress falls off rapidly away from the wall. Whether the viscosity at the centerline is finite or infinite may have little effect on any calculations. Thus the power law can be quite adequate in calculating such things as true shear rate at the wall for a non-Newtonian fluid.

In most cases η_0 can be estimated with more confidence than η_∞ . Mechanical degradation [36], static pressure effects [23], melt fracture [37], kinetic energy effects [2], or mechanical heating [38] may obscure high-shear-rate data. On the other hand, a reliable measure of η_0 usually is limited only by the patience of the investigator and the long-term stability of the system he is measuring. It follows that η_0 should precede η_∞ as a parameter in most models. Of course, many values of η_0 in the literature were not measured directly but extrapolated from other data according to an assumed model.

The various models suggest methods for deriving η_0 from data at finite shear rates. A plot of $1/\eta$ versus τ^a is recommended from the Ellis model, with a increasing from about 0.6 at $\log \eta_0 = 1$, to $a = 1.4$ at $\log \eta_0 = 5$. The intercept is $1/\eta_0$. For η_∞ a plot of $1/(\eta_0 - \eta)$ versus $1/\tau^2$ or $1/\dot{\gamma}$ is often used. The intercept, of course, is $1/(\eta_0 - \eta_\infty)$ in either case.

To the engineer a mathematical model for viscosity is a means to an end. Among other quantities, bulk flow rates in pipe and other conduits are usually desirable. The simple problem of deriving an equation for the velocity profile in laminar flow becomes a formidable task with some models. The popularity of the power law is due in good measure to its tractability to mathematical manipulations.

A radial velocity distribution in round pipes can be obtained by integration, making use of the linear stress distribution:

$$\tau = -\frac{r}{2} \frac{\Delta P}{L} \quad (7-40)$$

where $\Delta P/L$ is the pressure drop per unit length of pipe (usually a constant). Then

$$\int_0^u du = - \int_{\tau_w}^{\tau} \dot{\gamma} dr = \frac{2}{\Delta P/L} \int_{\tau_w}^{\tau} \dot{\gamma} d\tau \quad (7-38)$$

It can be seen that, in the absence of an explicit equation, the velocity distribution can be obtained by graphical or numerical integration.

All these manipulations assume that data corresponding to $\dot{\gamma}$ and τ are available. With data from most rotational viscometers this is nearly the case if $\dot{\gamma}$ and τ are evaluated at the geometric mean radius (see Sec. 7-7).

In a capillary viscometer the "true" rate of shear at the wall $\dot{\gamma}_w$ is related to that for a Newtonian fluid $(\dot{\gamma}_w)_a$ [39, 40]:

$$\dot{\gamma}_w = \frac{3+z}{4} (\dot{\gamma}_w)_a \quad (7-39)$$

where z is $d(\log \dot{\gamma})/d(\log \tau)$ at the point in question, $(\dot{\gamma}_w)_a = (4/\pi)(Q/r^3)$, and Q is the volume rate of flow.

Many authors have fitted capillary data to empirical equations using the "apparent" rate of shear $(\dot{\gamma}_w)_a$. Of course, this method is perfectly adequate as long as all operations are to be carried out in geometrically similar conduits. However, the use of such correlations in different geometries demands a rather laborious conversion of information to "true" rate of shear.

7-7 MEASUREMENT OF VISCOSITY

The parallel-plate geometry of Fig. 7-1 is seldom used in the routine measurement of viscosity. However, the behavior of capillary and rotational viscometers can be analyzed by using the same model despite the apparent differences in operation. In Fig. 7-16,

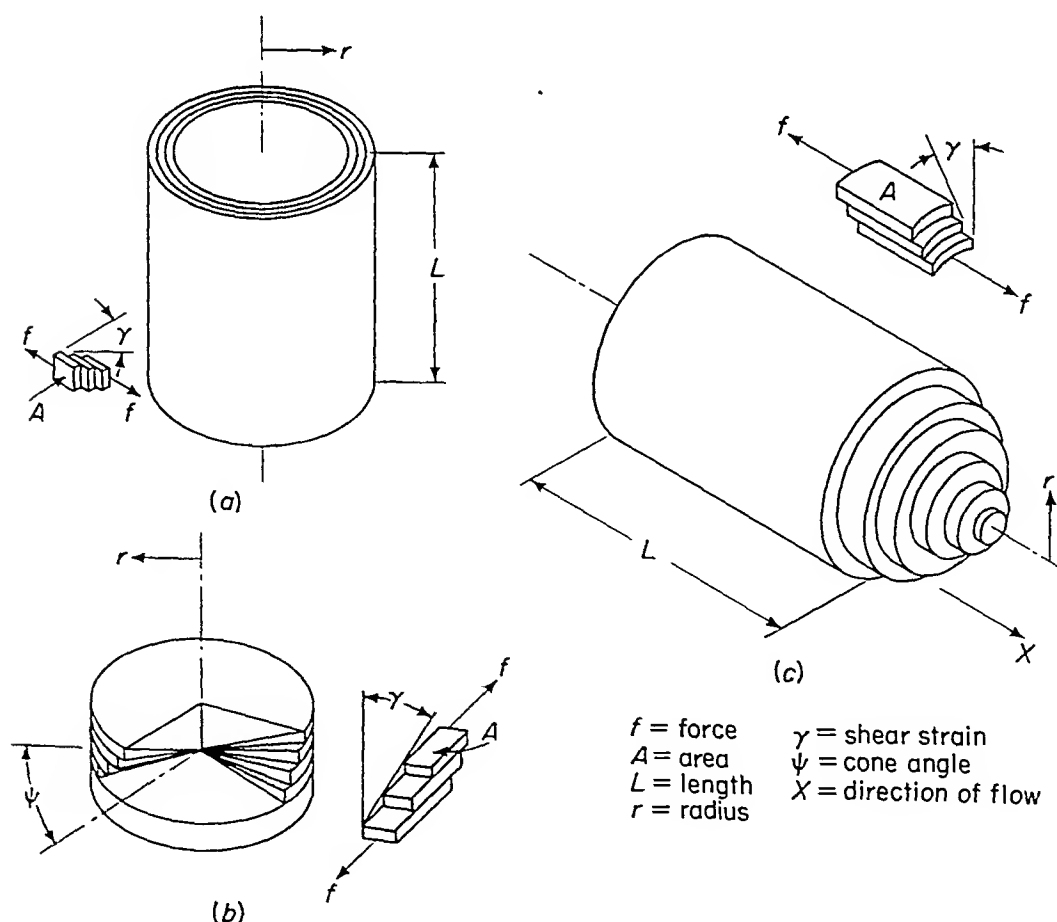


FIGURE 7-16

Laminar flow in (a) coaxial, (b) cone-plate, and (c) capillary geometry.

three typical viscometer geometries are pictured as moving liquid layers, so that the analogy with our definition is apparent. Only where inertial effects can be ignored is such a simplification possible. In the case of the rotational viscometers we measure a rate of rotation Ω in radians per second and a torque $\mathfrak{J}$ in Newton·meters ($1 \text{ N}\cdot\text{m} = 10^7 \text{ dyn}\cdot\text{cm}$). The average volumetric flow dV/dt and the pressure drop per unit length $\Delta P/L$ are measured in the capillary or pipe. The torque or pressure drop is *proportional to the shear stress*, and the rate of rotation or flow rate is *proportional to the rate of shear*. In calculating the stress, only geometric parameters enter into the proportionality constant. For the rate of shear, the model that relates stress to rate of shear may enter in. The expressions for stress and rate of shear will now be derived by considering, for each geometry, (1) a force balance involving shear stress at radius r ; (2) an expression for the shear γ_r , which can then be differentiated to give the rate of shear $\dot{\gamma}_r$, also at radius r ; and (3) insertion of a general expression relating $\dot{\gamma}$ to τ , the power-law model:

$$\dot{\gamma} = m\tau^z \quad (7-40)$$

Cup-and-Bob Viscometer (Figs. 7-16 and 7-17)

Bob radius = R_1 cm Bob length = L cm
 Cup radius = R_2 cm Rotational velocity of cup = Ω rad/s
 Measured torque = $\mathfrak{J}$, N·m (independent of radius)

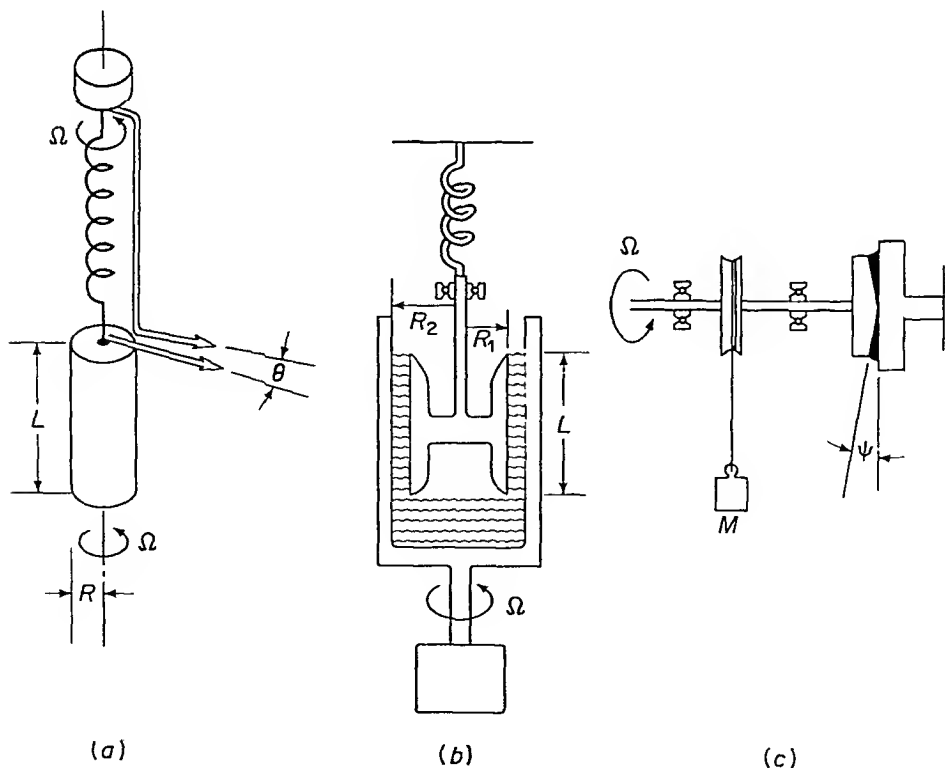


FIGURE 7-17

Rotational viscometers. (a) Extremely long cylinder in infinite volume of fluid, (b) coaxial cylinder (cup and bob), (c) cone-plate. Rate of rotation Ω is in radians per second.

- a. *Stress at radius r .* Consider a cylinder with radius $R_1 < r < R_2$. The force f dragging this cylinder of area $A = 2\pi rL$ is equal to the shear stress times the area. The torque is equal to rf .

$$f = 2\pi rL\tau_r = \frac{\mathcal{T}}{r} \quad (7-41)$$

$$\tau_r = \frac{\mathcal{T}}{2\pi r^2 L} \quad (7-42)$$

- b. *Shear and shear rate at radius r .* Regarded as a parallel-plate viscometer, the shear γ_r at radius r for a differential angular rotation of $d\theta$ is

$$\gamma_r = r \frac{d\theta}{dr} \quad (7-43)$$

The rate of shear becomes

$$\dot{\gamma}_r = \frac{d\gamma_r}{dt} = r \frac{d(d\theta/dr)}{dt} = r \frac{d^2\theta}{dr dt} = r \frac{d(d\theta/dt)}{dr} \quad (7-44)$$

For $d\theta/dt$ we can write Ω , the rotational velocity in radians per second, so that

$$\dot{\gamma}_r = r \frac{d\Omega}{dr} \quad (7-45)$$

- c. *Insertion of model.* With the cup rotating at Ω_c , we combine Eqs. (7-40), (7-42), and (7-45):

$$\dot{\gamma}_r = r \frac{d\Omega}{dr} = m\tau_r^z = m \left(\frac{\mathcal{T}}{2\pi r^2 L} \right)^z = C_z r^{-2z} \quad (7-46)$$

where

$$C_z = m \left(\frac{\mathcal{T}}{2\pi L} \right)^z \quad (7-47)$$

Assuming that m and z are independent of r and Ω , we can integrate from R_1 to r :

$$\int_0^{\Omega_r} d\Omega = C_z \int_{R_1}^r r^{-(2z+1)} dr \quad (7-48)$$

$$\Omega_r = \frac{C_z(r^{-2z} - R_1^{-2z})}{-2z} \quad (7-49)$$

At $\Omega_r = \Omega_c$,

$$\Omega_c = \frac{C_z(R_1^{-2z} - R_2^{-2z})}{2z} \tag{7-50}$$

and eliminating C_z between Eqs. (7-46) and (7-50) we get

$$\dot{\gamma}_r = \frac{2z\Omega_c r^{-2z}}{R_1^{-2z} - R_2^{-2z}} \tag{7-51}$$

Although Eqs. (7-42) and (7-51) can be applied at any value of r , the advantage of using a geometric-mean radius $r = (R_1 R_2)^{1/2}$ is apparent in Fig. 7-18. Equations (7-42) and (7-51) become

$$\tau_{gm} = \frac{3}{2\pi R_1 R_2 L} \tag{7-52}$$

$$\dot{\gamma}_{gm} = \frac{2z\Omega_c}{(R_2/R_1)^z - (R_1/R_2)^z} \tag{7-53}$$

Repetition of the derivation with the bob rotating at Ω_b and the cup stationary will give the same expressions with Ω_b replacing Ω_c . The two cases are not equivalent, however, because turbulence is induced in the system at lower values of Ω for the bob

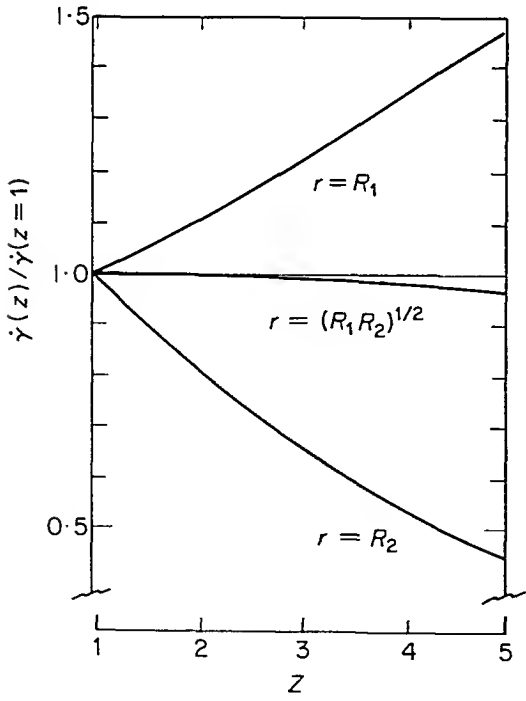


FIGURE 7-18
Relative change in rate of shear $\dot{\gamma}$ with increasing pseudoplastic behavior increasing $z = d(\ln \dot{\gamma})/d(\ln \tau)$ for $R_1/R_2 = 0.9$.

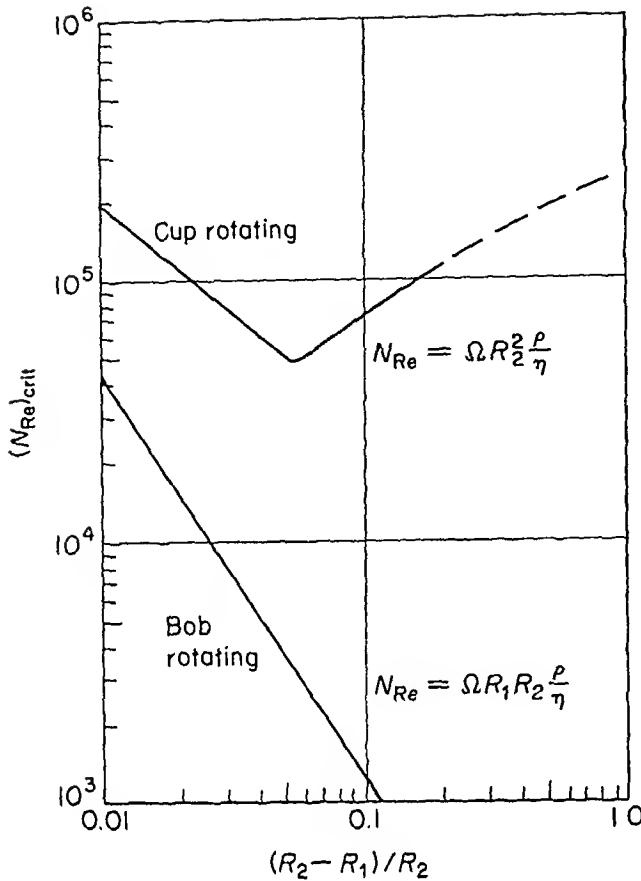


FIGURE 7-19
Onset of turbulence in coaxial cylinder geometry [41].

rotating than for the cup rotating. In the former case, the material on the surface of the bob is rotating faster than any other in the system. The centrifugal force eventually throws material outward and causes "Taylor turbulence," in which a helical path is followed by fluid particles and a series of toroids are formed in the annular space. The limiting values of stability for Newtonian fluids are correlated by using a Reynolds number as indicated in the diagram (Fig. 7-19).

A useful extension of the cup-and-bob viscometer is the bob rotating in an infinite amount of material (Fig. 7-17). Setting $R_2 = \infty$ and solving Eqs. (7-42) and (7-51) at R_1 , we have:

$$\tau_{R_1} = \frac{3}{2\pi R_1^2 L} \quad (7-54)$$

$$\dot{\gamma}_{R_1} = 2z\Omega_b \quad (7-55)$$

For a very long bob rotating in Newtonian fluid ($z = 1$) the rate of shear depends only on the rate of rotation and is independent of viscosity, length, and radius.

Cone and Plate Viscometer (Figs. 7-16 and 7-17)

Radius = R cm

Cone angle = ψ rad (preferably very small, say less than 0.1 rad; 1 rad = 57.296°)

Measured torque = $\mathfrak{J}$ N·m

Cone rotates at Ω rad/s

- a. *Stress at radius r .* Consider a ring of material of radius r and width dr . The force df dragging this ring past the ring below or above it is the shear stress times the area. The torque is equal to $r df$. It will be shown shortly that τ_r is independent of r , so that we can integrate from 0 to R to get the total torque.

$$df = 2\pi r \tau_r dr = \frac{d\mathfrak{J}}{r} \quad (7-56)$$

$$\int_0^{\mathfrak{J}} d\mathfrak{J} = \int_0^R 2\pi r^2 \tau_r dr \quad (7-57)$$

$$\tau_r = \frac{3\mathfrak{J}}{2\pi R^3} \quad (7-58)$$

- b. *Shear and rate of shear at radius r .* Regarded as a parallel-plate viscometer, the shear $d\gamma_r$ at radius r for a differential angular rotation of $d\theta$ is

$$d\gamma_r = \frac{r d\theta}{\text{thickness}} = \frac{r d\theta}{r\psi} = \frac{d\theta}{\psi} \quad (7-59)$$

The rate of shear also is independent of r :

$$\dot{\gamma}_r = \frac{d\gamma_r}{dt} = (\psi)^{-1} \frac{d\theta}{dt} = \frac{\Omega}{\psi} \quad (7-60)$$

This vindicates the statement made previously that τ_r should be independent of r .

Insertion of a model is not necessary, since Eq. (7-58) and (7-60) represent the desired solutions. The popularity of the cone-and-plate viscometer is due in no small measure to the simplicity of analysis that results from stress and rate of shear being independent of r .

Capillary Viscometer (Figs. 7-16 and 7-20)

Radius = R cm

Pressure drop = $\Delta P/L$ Pa/cm = $(P_1 - P_2)/(x_2 - x_1)$ by convention

Flow rate = Q cm³/s

- a. *Stress at radius r .* Consider a cylinder of material of radius r . The force f dragging this cylinder of area $A = 2\pi rL$ is equal to the shear stress times the area. The force also is equal to the pressure on the plug of radius r times the normal area of the plug πr^2 .

$$f = 2\pi rL\tau_r = \Delta P\pi r^2 \quad (7-61)$$

$$\tau_r = \frac{\Delta Pr}{2L} \quad (7-62)$$

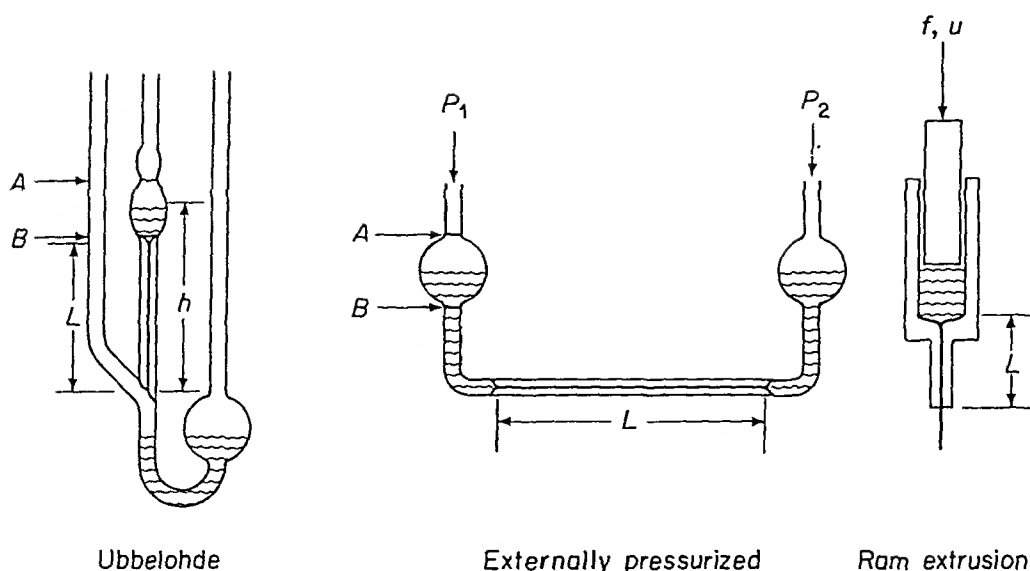


FIGURE 7-20

Capillary viscometers. Stress is proportional to h , $P_1 - P_2$, or ram force f . Rate of shear is proportional to $1/(\text{time of flow between marks})$ or to ram velocity u .

- b. *Shear and rate of shear at radius r .* Regarded as a parallel-plate viscometer, the shear γ_r at radius r for a differential translation dx in the x direction (parallel to the axis of the tube) is

$$\gamma_r = -\frac{dx}{dr} \quad (7-63)$$

The rate of shear becomes the velocity gradient, since the velocity is $u_r = (dx/dt)_r$:

$$\dot{\gamma}_r = \frac{d\gamma_r}{dt} = -\frac{d^2x}{dr dt} = -\left(\frac{du}{dr}\right)_r \quad (7-64)$$

- c. *Insertion of model.* We combine Eqs. (7-40), (7-62), and (7-64):

$$\dot{\gamma}_r = \left(-\frac{du}{dr}\right)_r = m \left(\frac{\Delta P}{2L}\right)^z r^z = \psi' r^z \quad (7-65)$$

where $\psi' = m(\Delta P/2L)^z$. Assuming m and z to be independent of r (not always a good assumption) and assuming $u = 0$ at $r = R$, we can integrate

$$\int_0^{u_r} -du = \psi' \int_R^r r^z dr \quad (7-66)$$

$$u_r = \frac{\psi'(R^{z+1} - r^{z+1})}{z+1} \quad (7-67)$$

At $r = 0$, $u = u_m$:

$$u_m = \frac{\psi'(R^{z+1})}{z+1} \quad (7-68)$$

Eliminating ψ' between Eqs. (7-67) and (7-68), we get

$$u_r = u_m \left[1 - \left(\frac{r}{R} \right)^{z+1} \right] \quad (7-69)$$

The average velocity $\bar{u}$ is given by the flow rate per unit cross-sectional area and also by integrating u_r for each ring of area $2\pi r dr$ and dividing by the total cross-sectional area:

$$\bar{u} = \frac{Q}{\pi R^2} = \int_0^R u_r \frac{2\pi r dr}{\pi R^2} \quad (7-70)$$

Using Eq. (7-69) for u_r , and integrating, we get $\bar{u}$ in terms of u_m :

$$\bar{u} = u_m \frac{z+1}{z+3} \quad (7-71)$$

Eliminating ψ' between Eqs. (7-65) and (7-68) yields

$$\dot{\gamma}_r = u_m \frac{(z+1)r^z}{R^{z+1}} \quad (7-72)$$

Substituting for u_m from Eqs. (7-70) and (7-71) gives the shear rate at any radius r in terms of the flow rate, the radius, and z :

$$\dot{\gamma}_r = \frac{(z+3)(Q)(r/R)^z}{\pi R^3} \quad (7-73)$$

At the wall, rate of shear and stress are at a maximum so that

$$\dot{\gamma}_w = \frac{(z+3)Q}{\pi R^3} \quad (7-74)$$

$$\tau_w = \frac{\Delta P R}{2L} \quad (7-75)$$

It can be seen that the true rate of shear at the wall differs from that calculated for a Newtonian fluid with the same flow rate Q by the factor $(z+3)/4$, often called the Rabinowitsch correction [42]. Actually, it is not necessary to invoke the power-law model as long as z is defined as $d(\ln Q)/d[\ln(\Delta P/L)]$ [43]. Cram and Whitwell

[39] pointed out that by referring the stress and rate of shear to a radius other than the wall, the correction factor could be minimized, but not so successfully as in the concentric cylinder geometry. At a radius that is 82.5% of the radius at the wall, stress and rate of shear are given by Eqs. (7-62) and (7-63) as:

$$\tau^+ = \frac{0.825(R \Delta P)}{2L} \quad (7-76)$$

$$\dot{\gamma}^+ = \frac{(z+3)Q(0.825)^z}{\pi R^3} \quad (7-77)$$

where reference radius is $R^+ = 0.825R$. The apparent rate of shear is

$$\dot{\gamma}_{app}^+ = \frac{4Q(0.825)}{\pi R^3} \quad (7-78)$$

Out to a value of $z = 4$ (Fig. 7-21), there is a maximum difference of only 3.2% between the apparent rate of shear (which requires no knowledge of z) and the corrected rate of shear. Unfortunately, most practicing rheologists ignore the advantage of this method and continue to refer measurements to wall conditions rather than to an intermediate radius. *Rheology* is the science of flow and deformation of matter.

7-8 ELASTIC LIQUIDS (NORMAL STRESSES AND MELT FRACTURE)

This extended treatment of one-dimensional, time-independent, non-Newtonian flow is an example of the complexity added by any new flow anomaly. When polymers are sheared, we have been assuming that the materials are purely viscous and have no rigidity, i.e., no shear modulus. This is far from the truth for polymer melts and even for some polymer solutions. The general treatment of combined viscous and elastic effects can be approached from the use of a time-dependent modulus (viscoelasticity, Chap. 8).

Some aspects of elastic behavior accompany and complicate attempts at steady-state measurements and will be mentioned here [37, 44, 45, 46].

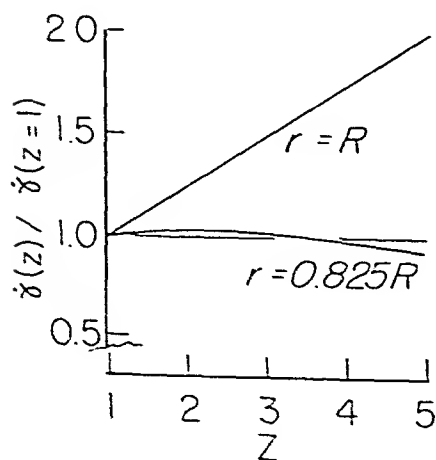


FIGURE 7-21

Change in true rate of shear $\dot{\gamma}$ compared to that for a Newtonian fluid ($z = 1$), $\dot{\gamma}_{app}$, at the wall and at an intermediate radius for tube flows.

If pressures normal to the direction of flow are measured in a cone-and-plate viscometer, the situations illustrated in Fig. 7-22 may arise. Generally speaking, such normal stresses increase with the rate of shear, the concentration of polymer in solution, the molecular weight of the polymer, and the amount of branching in the polymer. These stresses are a source of instability in rotational instruments, pushing the cone away from the plate and thus lowering the rate of shear at a given rotational speed. At some critical speed, a material exhibiting high normal stresses will relieve the situation by suddenly pulling out of the shearing zone, literally jumping out of a cup-and-bob instrument.

Relaxation of this elastic energy at the exit of the pipe results in an increase in diameter over that of the pipe or die (die swell) (Fig. 7-23). As the amount of elastic energy put into the polymer entering the pipe increases, the elastic limit is reached and a pulsating irregularity in flow appears (Fig. 7-23). Such "melt fracture" is a major limitation on extrusion processes. Changing the geometry of the pipe entrance to a more gradual constriction can raise the maximum flow rate at which these irregularities appear. However, slip-stick flow at the pipe wall and distortion at the exit are harder to cure. We can illustrate some features of elastic liquids by considering the flow process in a more general way than we did before. Consider the stresses that prevail on a particle of fluid in motion (Fig. 7-24). On each face we have three stresses (force/area). The nine stresses, each labeled τ_{ij} , form a stress tensor variously represented as τ_{ij} or

$$\tau_{ij} = \begin{pmatrix} \tau_{11} & \tau_{12} & \tau_{13} \\ \tau_{21} & \tau_{22} & \tau_{23} \\ \tau_{31} & \tau_{32} & \tau_{33} \end{pmatrix} \quad (7-79)$$

A torque balance about each axis can be used to show that it is necessary that $\tau_{21} = \tau_{12}$, $\tau_{13} = \tau_{31}$, and $\tau_{32} = \tau_{23}$. In the case of simple shear (Sec. 7-1) only τ_{21} and τ_{12} are involved. The normal stresses τ_{11} , τ_{22} , and τ_{33} will be recognized as the hydrostatic pressure for any fluid at rest or for a Newtonian fluid in motion.

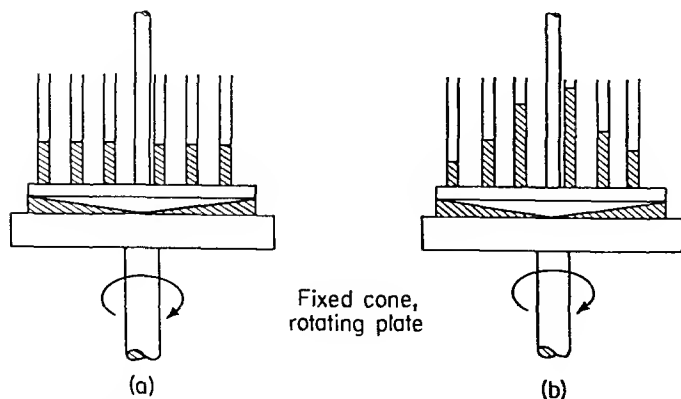


FIGURE 7-22

Relative normal pressures as shown by manometers inserted in stationary cone of cone-plate viscometer. (a) Purely viscous behavior; (b) viscoelastic behavior.

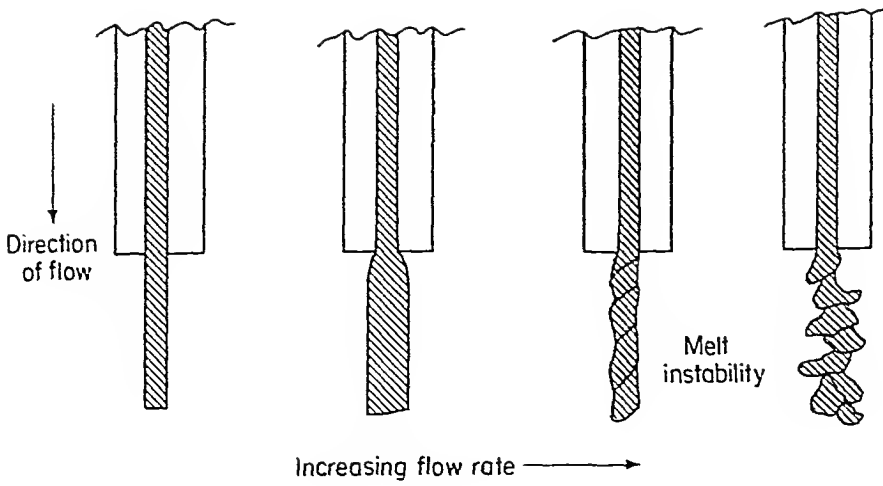


FIGURE 7-23

Typical stages in extrusion of polymer melt through capillary of diameter D_s . The die swell β is the extrudate diameter/ D_s .

The rate-of-strain tensor $\dot{\epsilon}_{ij}$ has nine components each in the same relative position as the stress with the same subscript. As before, $\dot{\epsilon}_{12} = \dot{\epsilon}_{21}$, $\dot{\epsilon}_{23} = \dot{\epsilon}_{32}$, and $\dot{\epsilon}_{13} = \dot{\epsilon}_{31}$. In a simple tensile test, for example, $\dot{\epsilon}_{11}$ would represent the rate of elongation responding along the axis where stress τ_{11} is acting. The rate of shear defined earlier is $2\dot{\epsilon}_{12}$. The most common viscous flow experiment is simple shearing flow. Experimentally, it is found that the following relationships are important (η and P_n are *not* constants) [47]:

$$\tau_{12} = \eta \dot{\gamma}_{12} \quad \text{viscosity} \quad (7-80)$$

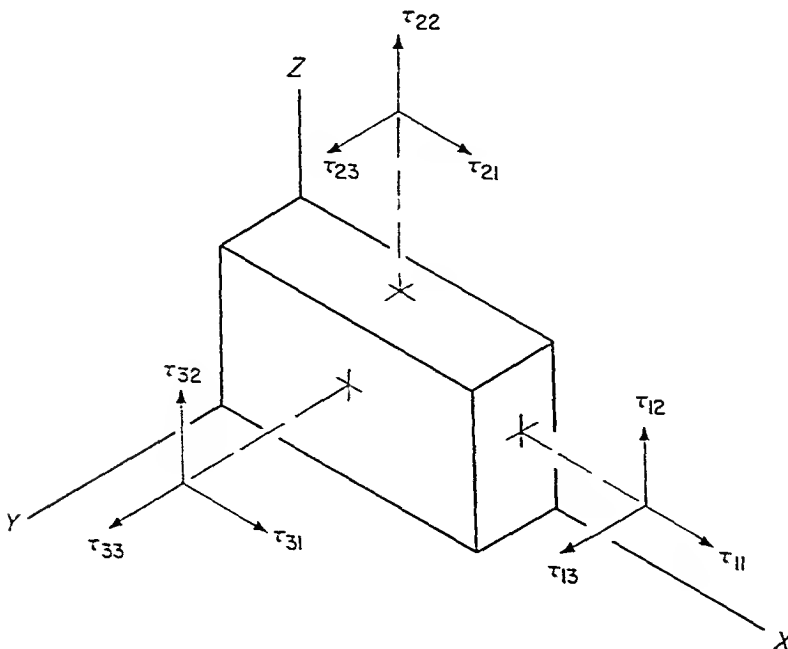


FIGURE 7-24

Stresses (force/area) exerted on fluid element.

$$\tau_{22} - \tau_{11} = P_n(\dot{\gamma}_{12})^2 \quad \text{first normal stress difference} \quad (7-81)$$

$$\tau_{33} - \tau_{22} \cong 0 \quad \text{second normal stress difference} \quad (7-82)$$

In a cone-plate viscometer, $\tau_{22} - \tau_{11}$ represents a force tending to push apart the cone and the plate. If the net force f on the cone of radius R is measured (above the force due to atmospheric pressure), the first normal stress difference can be calculated [47]:

$$\tau_{22} - \tau_{11} = \frac{2f}{\pi R^2} \quad (7-83)$$

Experimentally, the force f is affected by edge conditions, so that this formula is only approximate. The continuum mechanics of fluid dynamics can best be described using vector and tensor notation. Among the general references at the end of this chapter, many use this approach and apply it to polymer fabrication techniques such as extrusion and molding.

7-9 TURBULENT FLOW

A rather spectacular phenomenon is that of friction reduction in highly turbulent flow of dilute polymer solutions. Fabula has shown that small amounts of poly(ethylene oxide) in water reduce the pressure drop for a given flow rate to as little as one-fourth that for water alone [48]. In the experiments summarized in Fig. 7-25 it was found that the pressure drop, which is proportional to $(\tau_{12})_w$, steadily decreased as a high-molecular-weight ($M_v = 5.8 \times 10^6$) poly(ethylene oxide) was added. The Reynolds number N_{Re} is given by

$$N_{Re} = \frac{D\bar{u}\rho}{\eta} \quad (7-84)$$

where D = pipe diameter, cm

$\bar{u}$ = average velocity, cm/s

ρ = density, g/cm³

η = viscosity, poises (g/s·cm; 1 poise = 0.1 Pa·s)

For water in a 1-cm-diameter pipe, $D\rho/\eta \cong 100$, so the range of $\bar{u}$ represented in Fig. 7-25 corresponds to N_{Re} between 40,000 and 200,000. At the concentrations generally used for drag reduction, ordinary shear viscosity is relatively unaffected. But even at very low concentrations, *elongational viscosity* is increased dramatically. This can be demonstrated by the long, pituitous strings that can be drawn from solutions by dipping in an object and then withdrawing it rapidly. Other manifestations of the same phenomenon are the elastic recoil of stirred solutions when stopped suddenly and the inhibition of vortex formation in a draining vessel.

It is the high elongational viscosity that may change the rate of energy dissipation. Turbulent flow dissipates energy because of the exchange of momentum between fluid domains. These domains, or *eddies*, can be characterized by measuring

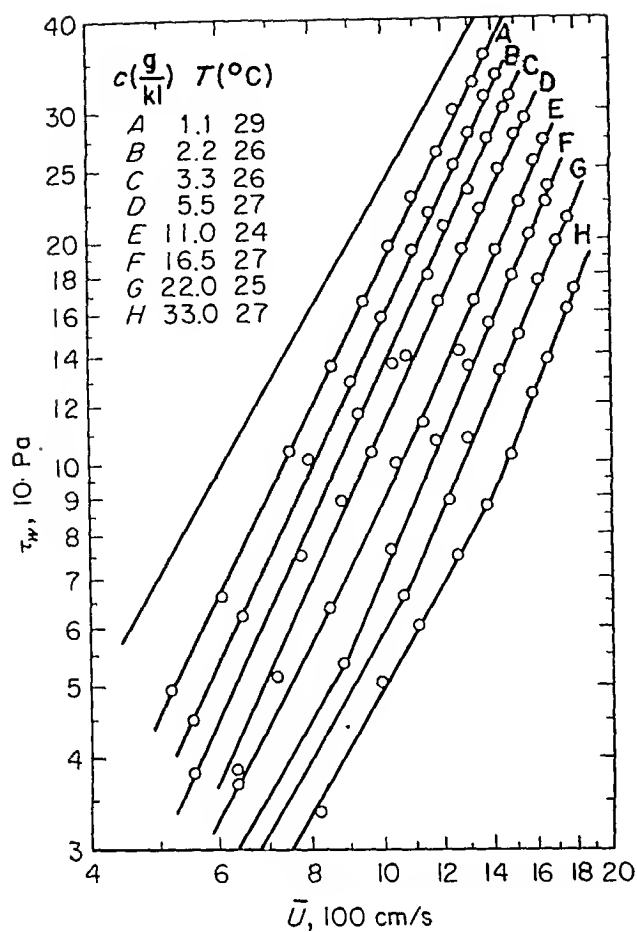


FIGURE 7-25

Decrease in stress (drag reduction) at constant average velocity $\bar{u}$ by addition of small amounts of high-molecular-weight poly(ethylene oxide) [48].

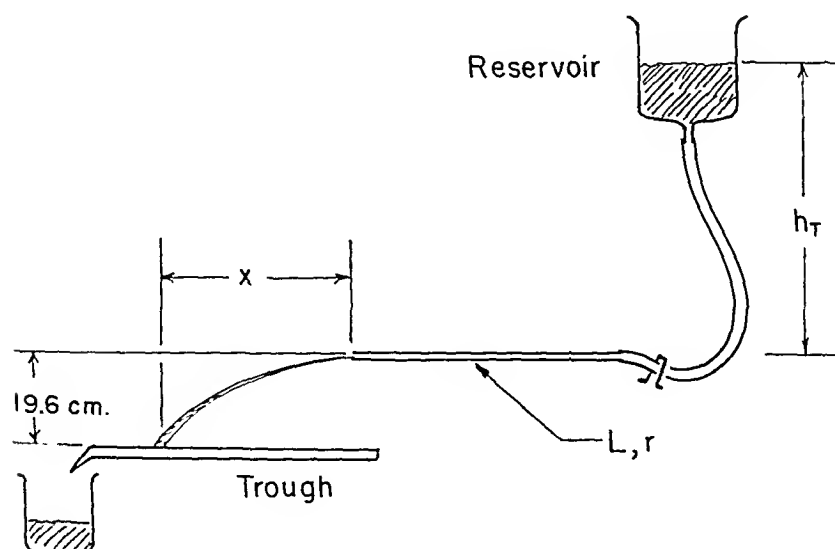


FIGURE 7-26

Apparatus for turbulent flow measurements.

TABLE 7-8
Turbulent Flow Measurement

Apparatus:	A 2000-cm ³ beaker + a precision-bore tube (Fig. 7-26)	
Typical data (water, 25°C):	Tube length, $L = 91.3$ cm	Jet distance, $x = 30.0$ cm
	Tube radius, $r = 0.15$ cm	Jet height, $y = 19.6$ cm
	Head, $h_T = 150$ cm	$\eta/\rho = 0.0090$ cm ² /s (25°C)
Equations:	Velocity, $u = 5.00x$ Reynolds number, $Re = 2ru/(\eta/\rho)$	
	Friction factor, $f = [(g/50)(h_T/x^2) - 0.35] (2r/L)$ (second term is kinetic energy correction)	
Calculated result (water):	$u = 150$ cm/s $Re = 5000$ $f = 0.0096$ (compared to expected value of 0.0094)	

velocity fluctuations in turbulent flow. In any system there will be a spectrum of eddy sizes. Turbulence is sometimes pictured as “eddies within eddies within eddies.” The withdrawal of material from the viscous sublayer along the wall is decreased by high elongational viscosity. Also, the small eddies throughout the conduit are decreased in intensity as the result of viscous damping.

Drag reduction has been suggested as a means of extending the distance that water from fire hoses can be discharged. For a fixed pressure drop, a smaller diameter hose will transmit the same flow of water enabling firemen to drag less weight per unit

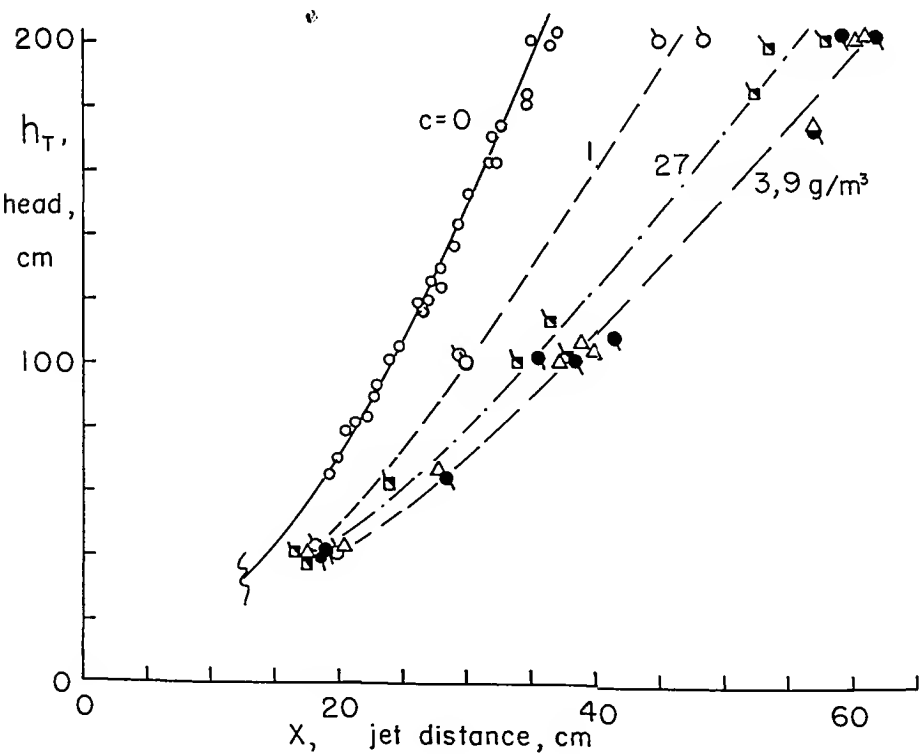


FIGURE 7-27
Typical flow data for dilute solutions of polyacrylamide. Results from several student groups are shown.

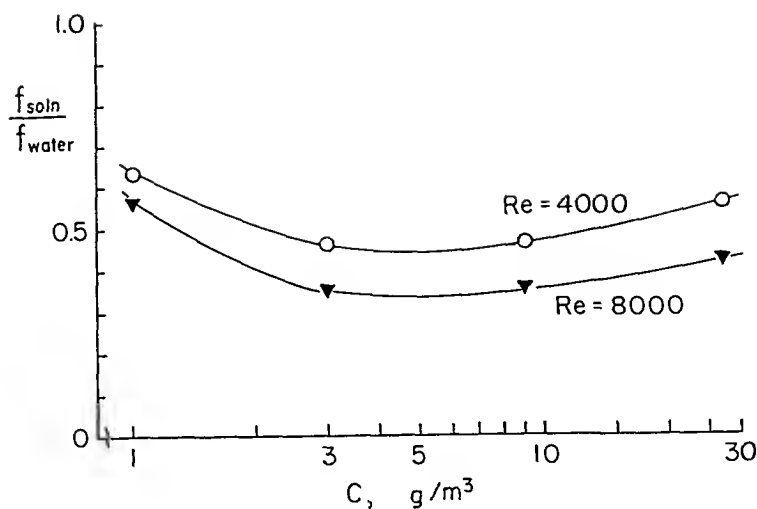


FIGURE 7-28

Data of Fig. 7-27 presented as ratio of friction factors at constant Reynolds number.

length when pulling hoses into buildings. Storm sewer capacity during temporary overloads can be increased by injection of polymers. A ship's speed can be increased by injection of a polymer solution at the bow.

For a quantitative demonstration [49], a simple apparatus (Fig. 7-26) consists of a reservoir that holds about 2000 cm³ of liquid and a flexible tube 200 cm long with an inside diameter of about 1 cm. This in turn is connected to a horizontal precision-bore tube. The efflux from the horizontal tube is allowed to fall freely a vertical distance of 19.6 cm into a trough and the horizontal jet distance x is measured. From simple mechanics, the average velocity in the tube u is related to x and to the time t for liquid to fall the 19.6 cm under the force due to gravity.

$$u = \frac{x}{t} = x \left(\frac{981}{39.2} \right)^{1/2} = 5.00x \quad (7-85)$$

If the total head is 150 cm, x will be around 30 cm at room temperature for water flowing through a tube with the dimensions listed in Table 7-8. When water is replaced by a dilute polymer solution, much larger values of x result. Typical results are shown in Fig. 7-27. In engineering calculations the Reynolds number and the friction factor are of interest (Table 7-8). The reduction in friction by a polyacrylamide solution is seen in Fig. 7-28. Some polymers that are effective are poly(ethylene oxide) (Polyox FRA, Union Carbide Corp.) and polyacrylamide (Separan MGL, Dow Chemical Co., and Polyhall 295, Stein, Hall and Co.).

PROBLEMS

- 7-1. The following data are for a narrow molecular weight fraction of poly(methyl methacrylate) in acetone at 30°C (density = 0.780 g/cm³):

c Concentration, g/100 ml	π Osmotic pressure, cm solvent	η_r Relative viscosity
0.275	0.457	1.170
0.338	0.592	
0.344	0.609	1.215
0.486	0.867	
0.896	1.756	1.629
1.006	2.098	
1.199	2.710	1.892
1.536	3.725	
1.604	3.978	2.330
2.108	5.919	2.995
2.878	9.713	

Plot appropriately and estimate $[\eta]$, k' (Huggins), $\bar{M}_n$, and the second virial coefficient. Include dimensions for each. Knowing that $[\eta]_\theta = 4.8 \times 10^{-4} M^{0.5}$ for this polymer in a theta solvent at 30°C , calculate from these data $(r_0^2)^{1/2}$, $(\bar{r}^2)^{1/2}$, and α , the expansion factor.

- 7-2. Two samples with narrow molecular weight distributions are prepared of a new polymer. Some measurements are made in acetone and in hexane.

Medium	Parameter	Sample A	Sample B
Acetone, 25°C	M_n (osmotic pressure)	8.50×10^4	Not run
	Second virial coeff.	Zero	
	Intrinsic viscosity	0.87 dl/g	1.32 dl/g
Hexane, 25°C	Intrinsic viscosity	1.25 dl/g	2.05 dl/g

(a) What is the M_n of sample B?

(b) What are the Mark-Houwink parameters (K' and a) in acetone and in hexane?

- 7-3. The system polyisobutylene-benzene has a theta temperature of 24°C . Describe how each of the quantities mentioned below would change for a given sample as the temperature is increased to 40°C from 24°C (increase, decrease, or no change). Explain why.

(a) Molecular weight measured by osmotic pressure

(b) Osmotic pressure of a 1-g/dl solution.

(c) Intrinsic viscosity.

(d) Ratio of M_w (light scattering) to M_n (osmotic pressure).

- 7-4. Three fractions are cut from a homopolymer. Each fraction has a very narrow molecular weight distribution. The following data are obtained. Fill in the missing data:

Fraction no.	Intrinsic viscosity at 25°C, dl/g		Melt viscosity at 200°C, Pa·s	Molecular weight, g/mol
	Solvent A	Solvent B		
1	1.2	2.0	?	1.3×10^5
2	1.8	3.6	4.0×10^5	?
3	2.5	?	?	5.6×10^5

- What is the actual radius of gyration (in nm) of fraction 1 in solvent B at 25°C?
- 7-5. Assuming that the rms end-to-end distance is an approximation to the diameter of the spherical, coiled polymer in dilute solution, compare the *volume* occupied by one molecule of polyisobutylene (mol wt = 10^6) (a) as a solid at 30°C ($\rho = 0.92 \text{ g/cm}^3$), (b) in a theta solvent (see Table 7-6), (c) in cyclohexane at 30°C (see Table 7-6).
- 7-6. From the information given below, calculate the ratio of the root-mean-square end-to-end distance in solvent A to that in solvent B for a polymer with a molecular weight of 1.00×10^7 .

Mol. wt	$[\eta]$ in A, dl/g	$[\eta]$ in B, dl/g
1.0×10^6	4.0	2.0
0.2×10^6	1.1	0.9
5.0×10^4	0.36	0.44

- 7-7. A typical laboratory capillary viscometer has a flow time t of water at 30°C of 200.0 s. The flow volume V is 5.0 cm^3 , capillary length L is 15 cm, and the average head $\bar{h}$ is $1.10L$. Estimate the diameter of the capillary disregarding end effects.
- 7-8. For poly(amyl zolate), assume that the hydrodynamic volume in a theta solvent at 30°C is 7.5 times that calculated for a chain of constant tetrahedral bond angle. If the repeat unit of four chain atoms has a molecular weight of 90, what is the molecular weight of the sample described by these data?

Theta solvent, 30°C	
c , g/dl	Viscosity, mPa·s
0.00	2.00
0.10	2.35
0.20	2.78
0.50	4.63
1.00	9.50

- 7-9. As a lecture demonstration it is desired to drop a plastic sphere (radius R , density $\rho = 1.200 \text{ g/cm}^3$) into a graduated cylinder full of a Newtonian solution (viscosity η , density $\rho_0 = 1.050 \text{ g/cm}^3$). According to Stokes the terminal velocity of the sphere $\bar{u}$ is given by:

$$\frac{2}{9}R^2g(\rho - \rho_0) = \eta\bar{u}$$

What values of R and η are reasonable for an effective experiment? The equation is valid only when the Reynolds number $N_{Re,p}$ is less than 0.1:

$$N_{Re,p} = \frac{2\bar{\eta}\rho_0 R}{\eta}$$

- 7-10. An empirical equation relating stress τ to rate of shear $\dot{\gamma}$ contains two constants, A and B :

$$\tau = \frac{A\dot{\gamma}}{1 + \sqrt{B\dot{\gamma}}}$$

Given that the zero-shear viscosity is 10 Pa·s for a certain sample and that the viscosity is 1.0 Pa·s at a stress of 10^3 Pa, calculate the viscosity at a rate of shear of $4 \times 10^3 \text{ s}^{-1}$.

- 7-11. Three Ubbelohde viscometers are constructed and their parameters are identified by subscripts 1, 2, and 3, respectively. Construction is such that $h_1 = h_2 = h_3$, $L_2 = L_3 = 2L_1$, and $D_1 = D_2 = 0.5D_3$. The volume of a power law liquid that flows through each in 100 s is measured (volumes V_1 , V_2 , and V_3). If $V_2/V_1 = \frac{1}{3}$, what is V_3/V_2 ?

- 7-12. For some polymer melts, viscosity plotted against shear stress on semilog paper gives a straight line.

- Write the corresponding equation for the rate of shear of a pseudoplastic melt in terms of the stress, the zero-shear viscosity, and the minimum number of remaining terms.
- Derive an equation for z as a function of stress where

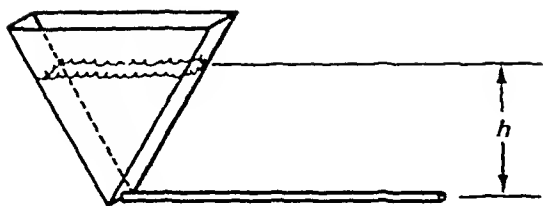
$$z = \frac{d(\ln \dot{\gamma})}{d(\ln \tau)}$$

- 7-13. The Ellis model for a non-Newtonian fluid can be written as

$$\frac{\eta_0}{\eta} - 1 = \left(\frac{\tau}{\tau_c} \right)^m$$

where η is the apparent viscosity at shear stress τ . Assuming that the shear rate can be given by $\dot{\gamma}_a = 4Q/\pi r^3$ and the stress by $\tau = \Delta Pr/2L$, calculate the flow rate in m^3/h through a long, vertical pipe draining under its own head: $\eta_0 = 10 \text{ Pa}\cdot\text{s}$, $\tau_c = 312 \text{ Pa}$, $m = 0.75$, $\rho = 1.0 \text{ g/cm}^3$, $r = 1.0 \text{ cm}$. Calculate a Reynolds number using the apparent viscosity.

- 7-14. A certain polymer solution can be characterized as a power-law fluid. Solution issues from a cylindrical storage tank through a horizontal capillary of length $L = 10.0 \text{ cm}$ and $r = 0.025 \text{ cm}$. The time is measured for the level in the cylinder to fall from 981.0 to 968.0 cm (40.0 s) and from 742.0 to 721.5 cm (90.0 s). Predict the time it will take for the level to fall from 550.0 to 540.0 cm.
- 7-15. Solve Prob. 7-14 assuming the reservoir has a rectangular cross section with two rectangular sides and two triangular sides. The apex of the triangles is at the entrance to the pipe.



7-16. The following mathematical model is proposed for non-Newtonian flow:

$$A\eta = \frac{1 + B\tau^z}{1 + C\tau^z}$$

- (a) Rewrite the equation in terms of $\dot{\gamma}$, τ , η_0 , η_∞ , C , and z .
 (b) If $C > B$, is the material dilatant or pseudoplastic? Why?

7-17. A polymer solution can be represented by the equation relating stress τ to rate-of-shear $\dot{\gamma}$:

$$\tau = 2.70 \times 10^2 \text{ (Pa)} (s^{0.635}) (\dot{\gamma}^{0.635})$$

What is the viscosity in mPa·s at a stress of 1000 Pa? Why is this equation likely to be misleading at very low shear rates? Is this solution dilatant, thixotropic, or rheopectic?

7-18. A coaxial viscometer with $R_2/R_1 = 1.10$, $R_1 = 2$ cm, $L = 5$ cm, is used to measure the viscosity of a fluid which follows the equation:

$$A\dot{\gamma} = \tau \left[1 + \left(\frac{\tau}{B} \right)^{1.5} \right]$$

where $A = 100$ Pa·s and $B = 1000$ Pa. When $\tau = 800$ Pa at the geometric-mean radius, what is (a) the steady-state torque $\mathfrak{T}$ in N·m, (b) the rotational speed in rpm, and (c) the ratio of rate of shear at the bob to that at the cup?

7-19. A fluid is forced by a pressure drop $P_2 - P_1$ to flow through two filters F_1 and F_2 . The filters are the same thickness and have the same total open area, but the pores of F_2 are half the diameter of those of F_1 . If the fluid is Newtonian, what is the ratio of the flows $Q_1:Q_2$ through F_1 and F_2 ? What is the ratio if the fluid follows a power law?

If the fluid is non-Newtonian, is there a possibility of the ratio $Q_1:Q_2$ being less than 1? Assume each filter is made up of a number of tubes of uniform length with no end effects. Assume all tubes of F_1 have the same diameter, etc.

7-20. Given the equation:

$$\dot{\gamma} = A\tau + B\tau^2 + C\tau^3 \quad \begin{aligned} A &= 1.0 \times 10^{-3} \\ B &= 2.0 \times 10^{-6} \\ C &= 3.0 \times 10^{-9} \end{aligned}$$

- (a) What is the zero-shear viscosity in Pa·s? ($\dot{\gamma}$, s^{-1} ; τ , Pa)
 (b) Calculate the *ratio* of flow rate (cubic centimeters per second) in a capillary viscometer at a stress of $\tau = 1000$ Pa compared to that at $\tau = 10$ Pa. For the capillary: $r = 0.05$ cm, $L = 10.0$ cm.

- 7-21. If 0.500 cm^3 of polymer described by the following model is placed in a parallel-plate viscometer with a plate separation of 0.0100 cm and a weight of 0.500 g is applied to the movable plate by appropriate pulleys, how far will the plate move in 10 s ? τ is in Pa.

$$\text{Model: } \dot{\gamma} = 2.00 \times 10^{-2} \tau^2$$

- 7-22. A power-law fluid flows through a slot of width W and height $2Y$ in the y direction under a pressure gradient $\Delta P/L$. Derive the following:

- (a) Stress τ_y as a function of y and $\Delta P/L$.
 (b) Velocity u_y as a function of $u_{\max}$, y , Y , and z .
 (c) Maximum rate of shear $\dot{\gamma}_w$ as a function of Q (flow rate, cm^3/s), W , Y , and z .

$$\dot{\gamma}_y = m\tau_y^z \quad W \gg Y$$

- 7-23. For a sample of poly(vinyl alcohol) in water at 21°C , the following data are obtained:

Concentration, g/dl	0	2.0	3.0	4.0	6.0	7.0	10.0
Viscosity, mPa·s	1.00	10.0	28.0	58.0	240	550	4000

From a Martin's plot estimate $[\eta]$.

- 7-24. In order to simplify end corrections in a cup-and-bob viscometer, the ends can be conical. If each end of the bob is the cone of a cone-plate viscometer, what is the ratio of torque due to the ends of the bob to the torque due to flow in the annulus in the cylindrical part? Assume a bob of length L and radius KR , a cup of radius R , and a cone angle of $1 - K$. Assume a Newtonian fluid and refer torque in the annulus to the geometric-mean radius.
- 7-25. For a Bingham plastic, qualitatively, what unusual feature must a velocity profile in pipe flow exhibit? In a cup-and-bob viscometer, what discontinuity might be expected in the flow field for the same model? In a cone-plate viscometer, would any discontinuities be expected?
- 7-26. Estimate the parameters for Eqs. (7-31) and (7-32) for the flow curve at 260°C (polystyrene) in Fig. 7-13.
- 7-27. What is the maximum shear rate that one could use in a cone-plate viscometer with a Newtonian liquid of $100 \text{ Pa}\cdot\text{s}$ if the adiabatic heating rate is to be kept below $0.01^\circ\text{C}/\text{min}$? Assume a density of $0.95 \text{ g}/\text{cm}^3$ and a specific heat of $2.5 \text{ J}/\text{g}\cdot^\circ\text{C}$.

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8

MECHANICAL PROPERTIES AT SMALL DEFORMATIONS

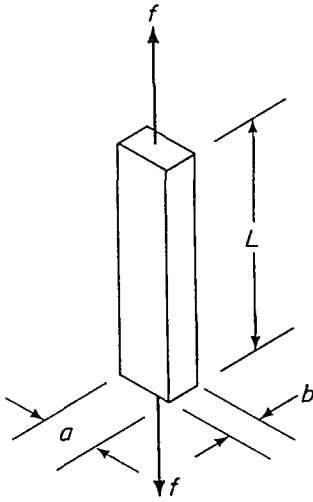
The mechanical properties of amorphous polymers at small deformations have been one of the most fruitful areas for theoreticians. The equation for equilibrium elasticity of cross-linked amorphous networks is one of the triumphs of statistical mechanics. Similarly, linear viscoelasticity has yielded to generalizations that are mainly empirical but have a theoretical explanation. On the other hand, partly crystalline and heterogeneous, reinforced materials are not so well correlated, even at small deformations. The situation regarding ultimate properties of all materials (tensile strength, fatigue strength, impact strength, burst strength) is even more nebulous, although there is a vast store of empirical knowledge.

8-1 ELASTICITY IN VARIOUS GEOMETRIES

In Chap. 7 we looked at polymer melts and solutions as liquids, and only in the later sections did we introduce the idea of elasticity. While it is useful to think of these as elastic liquids, rubber, glass, and materials of low flow under stress are more profitably generalized as elastic *solids* whose characteristic parameters are somewhat time-dependent. Some familiar mechanical properties are summarized in Table 8-1. Other quantities are used also. For example, "true" stress is sometimes used as force/(actual area) rather than the more conventional definition of force/(original area). In ordinary calculations for steel, wood, and other materials of construction, the materials are regarded as linearly elastic and a constant value is assumed for the modulus. We shall use some of these formulas where the moduli are functions of time of stress application or rate of stress application.

TABLE 8-1
Mechanical Deformation—Terminology and Formulas

Tension:



Original dimensions L_u, a_o, b_o

$$\sigma = \text{tensile stress} = \frac{f}{ab} = \text{force/area}$$

$$\epsilon = \text{elongation} = \frac{\Delta L}{L_u} = \alpha - 1$$

$$E = \text{Young's modulus} = \frac{\sigma}{\epsilon}$$

$$J = \text{compliance} = \frac{\epsilon}{\sigma}$$

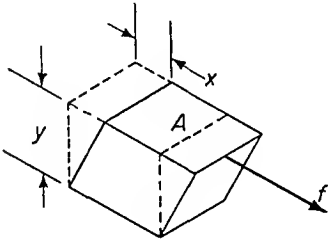
$$\nu = \text{Poisson's ratio} = \frac{-d(\ln a)}{d(\ln L)} = \frac{-d(\ln b)}{d(\ln L)}$$

$$\tau = \text{shear stress} = \frac{f}{A}$$

$$\gamma = \text{shear strain} = \frac{x}{y}$$

$$G = \text{storage (shear) modulus} = \frac{\tau}{\gamma}$$

Shear:



Bulk:

P = hydrostatic pressure, V = volume

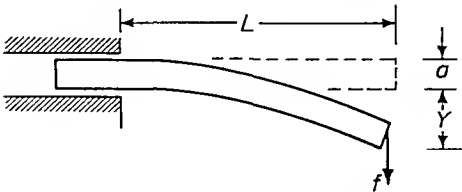
$$B = \text{bulk modulus} = \frac{\Delta P}{\Delta V/V_o} = \text{compressibility}^{-1}$$

Isotropic materials:

$$E = 2G(1 + \nu) = 3B(1 - 2\nu) \quad (8-1)$$

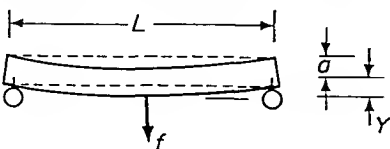
$\nu = 0.5$ for incompressible liquids, most rubbers

Cantilever beam, end-loaded (b = width):



$$Y = \frac{4fL^3}{ba^3E} \quad (8-2)$$

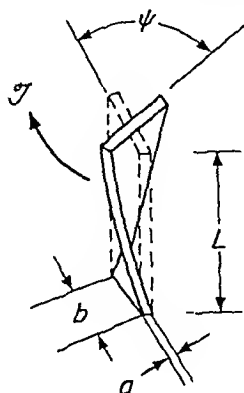
Simple beam, center-loaded (b = width):



$$Y = \frac{fL^3}{4ba^3E} \quad (8-3)$$

TABLE 8-1
Mechanical Deformation—Terminology and Formulas (*Continued*)

Beam in torsion (torque $\mathfrak{J}$; angle of twist, ψ' rad):



$$\frac{\psi'}{\mathfrak{J}} = \frac{16L}{ba^3 G\mu} \quad (8-4)$$

$$\mu = 5.333 - 3.36 \frac{a}{b} \quad 0 < \frac{a}{b} < 0.5$$

From the definition of Poisson's ratio, in Table 8-1 it is easily seen that when the volume of a material ($V = abL$) does not change on stretching, $\nu = 0.5$.

$$V = abL \quad (8-5)$$

$$\frac{d(\ln V)}{d(\ln L)} = \frac{d(\ln a)}{d(\ln L)} + \frac{d(\ln b)}{d(\ln L)} + 1 \quad (8-6)$$

If the changes in a and b with L are proportionately the same and V does not change with L ,

$$2 \frac{d(\ln a)}{d(\ln L)} + 1 = 0 \quad \nu = 0.5 \quad (8-7)$$

Hooke's law, the direct proportionality between stress and strain in tension or shear, is often assumed. It will be shown that for cross-linked, amorphous polymers above T_g a nonlinear relationship can be derived theoretically. For such materials $\nu = 0.5$. When ν is not 0.5, it is an indication that voids are forming in the sample or that crystallization is taking place. In either case, neither the theoretical equation nor Hooke's law generally applies.

8-2 RUBBER ELASTICITY [1]

The first law of thermodynamics states that the change in internal energy of an isolated system ΔE is equal to the heat added to the system Q less work done by the system W

$$\Delta E = Q - W \quad (8-8)$$

From the second law we know that an increment of entropy dS is equal to an increment of heat dQ added reversibly at temperature T .

$$dS = \frac{dQ_{\text{rev}}}{T} \quad (8-9)$$

If we stretch a piece of rubber with force f a distance dL , we also do work involving pressure and volume:

$$dW = P dV - f dL \quad (8-10)$$

Combining all these, we have [differentiating Eq. (8-8)]

$$dE = T dS - P dV + f dL \quad (8-11)$$

With the introduction of several assumptions, the chief one being that V does not change greatly on stretching (a good assumption for rubber), the "thermodynamic equation of state" for rubber is

$$f = \left(\frac{\partial E}{\partial L} \right)_{T, V} + T \left(\frac{\partial f}{\partial T} \right)_{P, \alpha} \quad (8-12)$$

$$\text{and } \left(\frac{\partial f}{\partial T} \right)_{P, \alpha} = - \left(\frac{\partial S}{\partial L} \right)_{T, V} \quad (8-13)$$

where $\alpha = L/L_u$, the ratio of length to unstretched length at T .

Changes in ΔE for a system are identified with changes in temperature and with energy stored by bond bending and stretching. Changes in ΔS are changes due to differences in conformation. In this respect the concept of entropy as a measure of probability is useful. If a string is stretched tightly between two points, there is only one arrangement for the string in space to satisfy the condition. If the two points are moved together, the rest of the string can accommodate the change by numerous conformations in space. In other words, if all conformations in space are equally likely, the stretched condition is the least probable (only one way of being achieved, lowest entropy) and the two ends together is the most probable (many ways of being achieved, highest entropy).

The "ideal" rubber should respond to an external stress *only* by uncoiling, that is, $\partial E / \partial L = 0$. Experiments in which f , L , and T are varied confirm that for many amorphous, cross-linked materials above T_g , $\partial E / \partial L$ is very small (Fig. 8-1). Below T_g , we have said that polymer segments cannot deform in the time scale in which T_g was measured, so $\partial S / \partial L = 0$. In a glass we expect external stresses to be countered by bond bending and stretching.

Now, for an ideal rubber we have

$$f = -T \left(\frac{\partial S}{\partial L} \right)_{T, V} \quad (8-14)$$

According to Boltzmann the entropy of a system in a given state with respect to a reference state entropy is related to the ratio of the probability of that state Ω_2 to that in the reference state Ω_1 by the equation

$$\Delta S = k \ln \frac{\Omega_2}{\Omega_1} \quad (8-15)$$

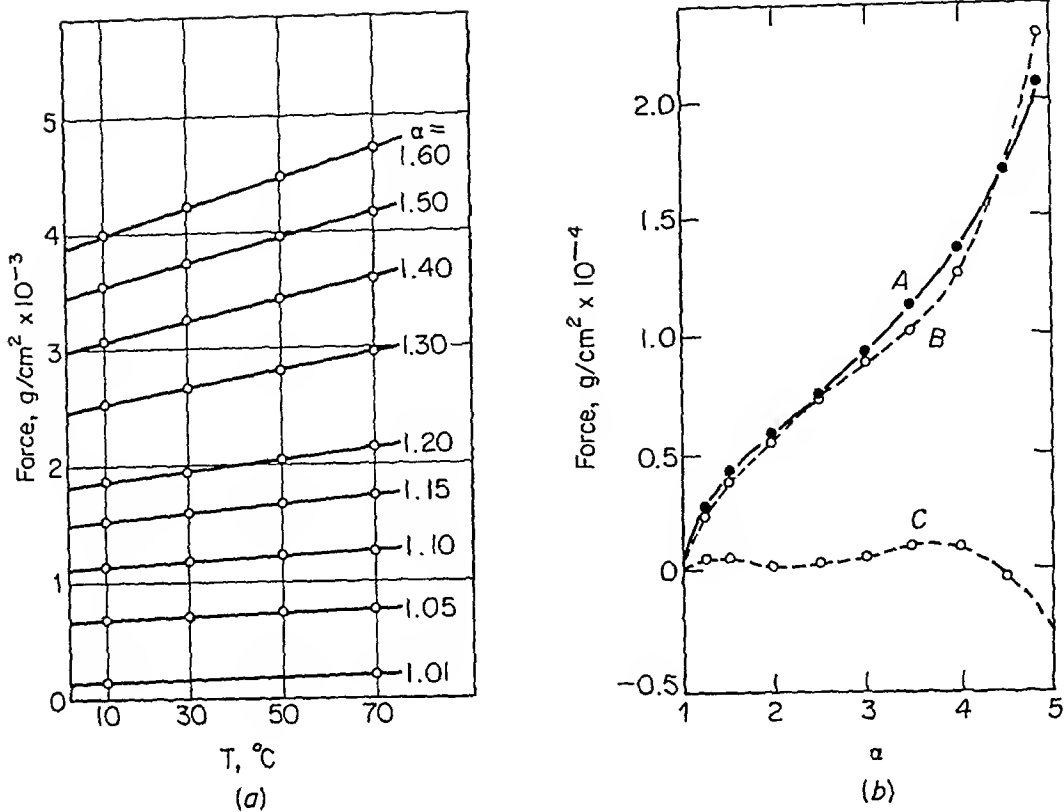


FIGURE 8-1

(a) Force vs. temperature at constant values of α for sulfur-cross-linked natural rubber [2]. (b) Force of retraction, A ; $(\partial E / \partial L)_T, V$, B ; and $-T(\partial S / \partial L)_T, V$, C , obtained by using Eqs. (8-12) and (8-13) [2]. (Reproduced by permission, R. L. Anthony et al., *J. Phys. Chem.*, 46:826, © 1942, the Williams and Wilkins Company, Baltimore, Maryland.)

where k is the Boltzmann constant, the gas constant per molecule. What we need to know, then, is how does the probability of a polymer segment quantitatively decrease when it goes from a more probable state to a less probable state? The picture we have is a polymer segment that is part of a loose network. When we stretch the whole piece of rubber, we move the ends of the segment to new positions in the same proportion as we do the whole piece (an "affine" deformation). Because these chains are part of a network, the chain ends cannot diffuse to more probable positions. The rubber cannot "relax." Only removal of the external stress will allow the chain ends to return to their original distribution. The derivation of a distribution of chain lengths follows the same pattern as the random-flight problem. Let us now look at the probability $\Omega(x, y, z)$ that a polymer segment has one end fixed at the origin of a coordinate system (Fig. 8-2) and the other end at (x, y, z) . A simple model for this probability is one in which Ω decays exponentially with the square of the distance from the origin.

$$\Omega(x, y, z) = \left(\frac{\beta^2}{\pi} \right)^{3/2} \exp [-\beta^2(x^2 + y^2 + z^2)] \quad (8-16)$$

This is a Gaussian distribution. Here $\beta = (\frac{3}{2})^{1/2} n^{-1/2} a^{-1}$ and n is the number of bonds each of length a . Of course, this will apply only at small deformations. After all, the polymer can be elongated only to its length of n bonds, whereas this model predicts

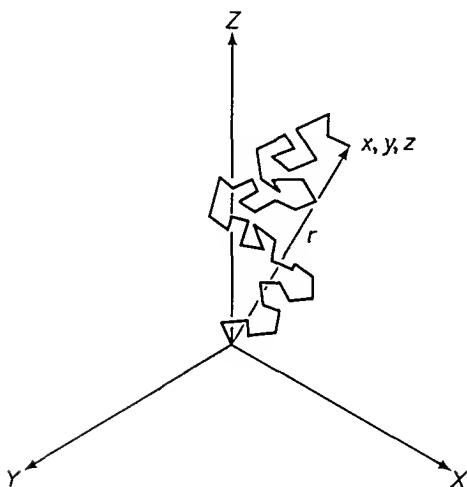


FIGURE 8-2

Random flight in three dimensions with resultant distance traveled equal to r .

a small but real probability of chain lengths increasing without limit. From Eq. (7-6), $\overline{r_0^2} = na^2$, and from geometry $r^2 = x^2 + y^2 + z^2$. Equation (8-16) is consistent with the idea that $\overline{r_0^2}$ is the most probable value of r^2 , even though the most probable value for r , as well as for x , y , and z , is zero.

If we change the overall dimensions of the sample so that now $x_2 = \alpha_x x$, $y_2 = \alpha_y y$, and $z_2 = \alpha_z z$, the ratio of the probability in perturbed state 2 to that in unperturbed state 1 can be expressed as

$$\ln \frac{\Omega_2}{\Omega_1} = -\beta^2 [(\alpha_x^2 - 1)x^2 + (\alpha_y^2 - 1)y^2 + (\alpha_z^2 - 1)z^2] \quad (8-17)$$

But initially in our sample, chain ends were randomly oriented in all directions, so we can replace x^2 , y^2 , and z^2 each by their average value, $\overline{r_0^2}/3$, giving for each chain [Eq. (8-15) and (8-17)]:

$$\Delta S = S_2 - S_1 = k \ln \frac{\Omega_2}{\Omega_1} = -k \frac{3}{2na^2} \frac{\overline{r_0^2}}{3} (\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) \quad (8-18)$$

$$\text{or} \quad \Delta S = -\frac{k}{2} (\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3)$$

Let us say that we have ζ effective chains in our system, or better, segments with ends that cannot move freely because they are tied in junctions (cross-links). Then, for the entire system

$$\Delta S = -\frac{k\zeta}{2} (\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) \quad (8-19)$$

$$\text{also} \quad f = -T \left(\frac{\partial \Delta S}{\partial L} \right)_{T, V} = -\frac{T}{L_u} \left(\frac{\partial \Delta S}{\partial \alpha_x} \right)_{T, V} \quad (8-20)$$

If rubber is stretched in the x direction and the total volume remains constant,

$$\alpha_x \alpha_y \alpha_z = 1 \quad \text{and} \quad \alpha_y^2 = \alpha_z^2 = \frac{1}{\alpha_x} \quad (8-21)$$

Then

$$f = \frac{kT\xi}{L_u} \left[\alpha_x - \left(\frac{1}{\alpha_x} \right)^2 \right] \quad (8-22)$$

If retractive force per unit area $\sigma = f/A_u$, where A_u is the *original* cross-sectional area, and *original* volume $V_u = L_u A_u$, then

$$\sigma = kT \frac{\xi}{V_u} \left[\alpha_x - \left(\frac{1}{\alpha_x} \right)^2 \right] = RTN \left(\alpha - \frac{1}{\alpha^2} \right) \quad (8-23)$$

where R is the gas constant per mole and N is the moles of polymer chains per unit volume. For example, suppose we have cross-linked rubber composed of segments with molecular weight 10,000 and an overall density of 1 g/cm³. What is σ at 100% elongation ($\alpha_x = 2$) at 25°C?

$$N = \frac{1 \text{ g}}{\text{cm}^3} \frac{\text{g} \cdot \text{mol}}{10,000 \text{ g}} \frac{6.02 \times 10^{23} \text{ molecules}}{\text{g} \cdot \text{mol}} = 6.02 \times 10^{19} \frac{\text{molecules}}{\text{cm}^3}$$

where $T = 298 \text{ K}$

$$k = 1.38 \times 10^{-9} \text{ J/K} \cdot \text{mol}$$

$$\sigma = 1.38 \times 10^{-9} \times 298 \times 6.02 \times 10^{19} (2.00 - 0.25)$$

$$= 0.433 \text{ J/cm}^3 = 433 \text{ kPa} = 4.33 \times 10^6 \text{ dyn/cm}^2$$

Since $1 \text{ dyn/cm}^2 = 1.450 \times 10^{-5} \text{ lb/in}^2 \text{ (psi)} = 1.02 \times 10^{-6} \text{ kg/cm}^2$,

$$\sigma = 62.8 \text{ psi} = 4.42 \text{ kg/cm}^2$$

Equation (8-23) has been confirmed for rubbery materials when viscous effects can be made small. One way to decrease viscous effects is to swell the rubber to a new volume V_s by immersion in a low-molecular-weight solvent. Polymer molecules now are "lubricated," so that viscous drag is minimized. Two other phenomena should be taken into account. In the first place, polymer segments at chain ends do not contribute to the modulus, because they are not restrained at one end. It is necessary to subtract from the chain density N the quantity $2\rho/M_n$ representing the density of chain ends per unit volume. The original number-average molecular weight before cross-linking M_n and the density ρ are required. In the second place, the deviation from Gaussian statistics at large deformations can be taken into account by using an additional constant C_2 to give the "Mooney-Rivlin" form of the equation. Assembled into one equation, we then get [3]:

$$\sigma = \left[\left(N - \frac{2\rho}{M_n} \right) RT + \frac{2C_2}{\alpha} \right] \left(\alpha - \frac{1}{\alpha^2} \right) \left(\frac{1}{v_2} \right)^{1/3} \quad (8-24)$$

where σ is based on the original, *unswollen* cross section, α is the ratio of length to *swollen*, unstretched length, and $v_2 = V_u/V_s$. An example of natural rubber swollen in benzene (Fig. 8-3) gives a value for N that is relatively constant and values of C_2 that decrease as v_2 decreases. Many unswollen, homogeneous rubbers (gum or unfilled materials) are better represented by the empirical equation of Martin, Roth, and Stiehler [5]:

$$\ln \frac{\sigma \alpha^2}{\alpha - 1} = \ln \Lambda + \lambda \frac{\alpha^2 - 1}{\alpha} \quad (8-25)$$

The constant λ normally has a value of 0.38 ± 0.02 . The results for two samples of rubber (Fig. 8-4) show that this equation applies in compression as well as tension.

The differences between Eqs. (8-23), (8-24), and (8-25) (compared in Fig. 8-5) are quantitative rather than qualitative.

8-3 VISCOELASTICITY-MAXWELL MODEL

Although we have shown that stress σ is not directly proportional to strain, $\epsilon = \alpha - 1$, for the ideal rubber, it is convenient in dealing with very small deformations of ma-

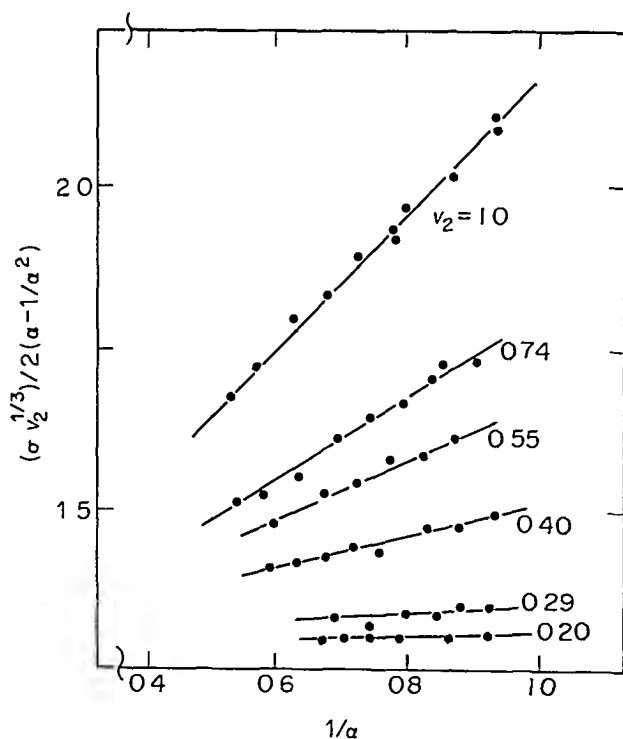


FIGURE 8-3

Stress-strain data for cross-linked natural rubber swollen to various degrees in benzene plotted according to Eq. (8-24) [4].

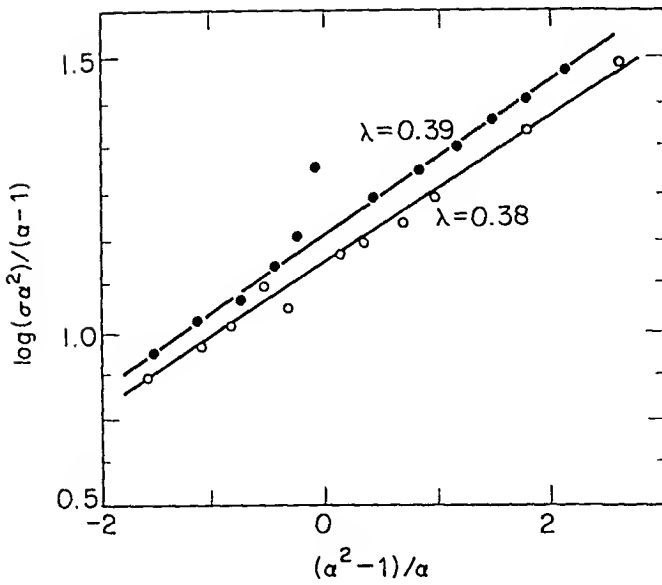


FIGURE 8-4

Plots for two samples of cross-linked natural rubber according to Eq. (8-25) [6]. Stress is in kg/cm^2 .

materials with both elastic and viscous nature to combine a linear, Hookean stress-strain relationship with a linear, Newtonian viscous relationship in order to illustrate the behavior of real materials. First, we introduce a simple mathematical model, the Maxwell element. Even though this model is inadequate for quantitative correlation of polymer properties, it illustrates the qualitative nature of real behavior. Furthermore, it can be generalized by the concept of a distribution of relaxation times so that

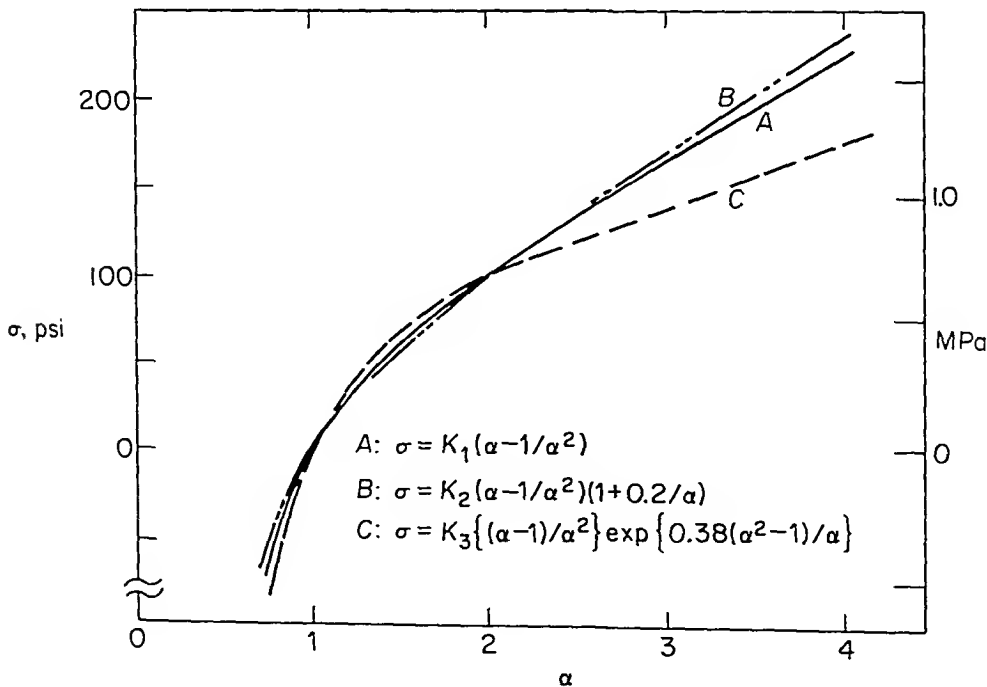
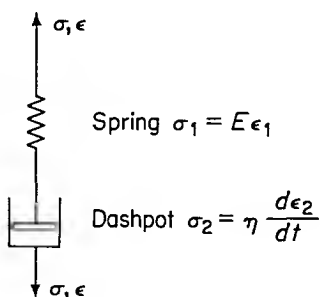


FIGURE 8-5

Equations compared with condition imposed that $\sigma = 100$ psi at $\alpha = 2$.

it becomes adequate for quantitative evaluation. Maxwell's element is a simple one combining one viscous parameter and one elastic parameter. Mechanically, it can be visualized as a Hookean spring and a Newtonian dashpot in series:



where σ is the stress, ϵ is the elongation, $d\epsilon/dt$ is rate of elongation with time, E is the Hooke's law constant or Young's modulus, and η is a viscosity coefficient. From the diagram it is apparent that

$$\sigma = \sigma_1 = \sigma_2 \quad \epsilon = \epsilon_1 + \epsilon_2$$

$$\text{and } \frac{d\epsilon}{dt} = \frac{d\epsilon_1}{dt} + \frac{d\epsilon_2}{dt} = \frac{1}{E} \frac{d\sigma}{dt} + \frac{\sigma}{\eta} \quad (8-26)$$

The behavior of this model in four experiments is considered now.

Creep

A fixed stress σ_0 is applied to the sample at time $t = 0$ (Fig. 8-6a). We desire the elongation as a function of time $\epsilon(t)$. With stress constant in the spring, ϵ_1 is constant and $d\epsilon_1/dt = 0$.

$$\frac{d\epsilon}{dt} = \frac{d\epsilon_1}{dt} + \frac{d\epsilon_2}{dt} = \frac{\sigma_0}{\eta} \quad (8-27)$$

$$\int_{\epsilon_0}^{\epsilon(t)} d\epsilon = \frac{\sigma_0}{\eta} \int_0^t dt \quad (8-28)$$

$$\epsilon(t) = \epsilon_0 + \frac{\sigma_0 t}{\eta} = \sigma_0 \left(E^{-1} + \frac{t}{\eta} \right) \quad (8-29)$$

Often, it is useful to express the results as a time-dependent *compliance* $J(t)$, where

$$J(t) = \frac{\epsilon(t)}{\sigma_0} = E^{-1} + \frac{t}{\eta} \quad (8-30)$$

The *linear viscoelastic region* is the region where $J(t)$ is independent of σ_0 or, more generally, where the dependence is expressible by an exact relationship like Eq. (8-23). It can be seen from the diagram that when the stress is removed, only the

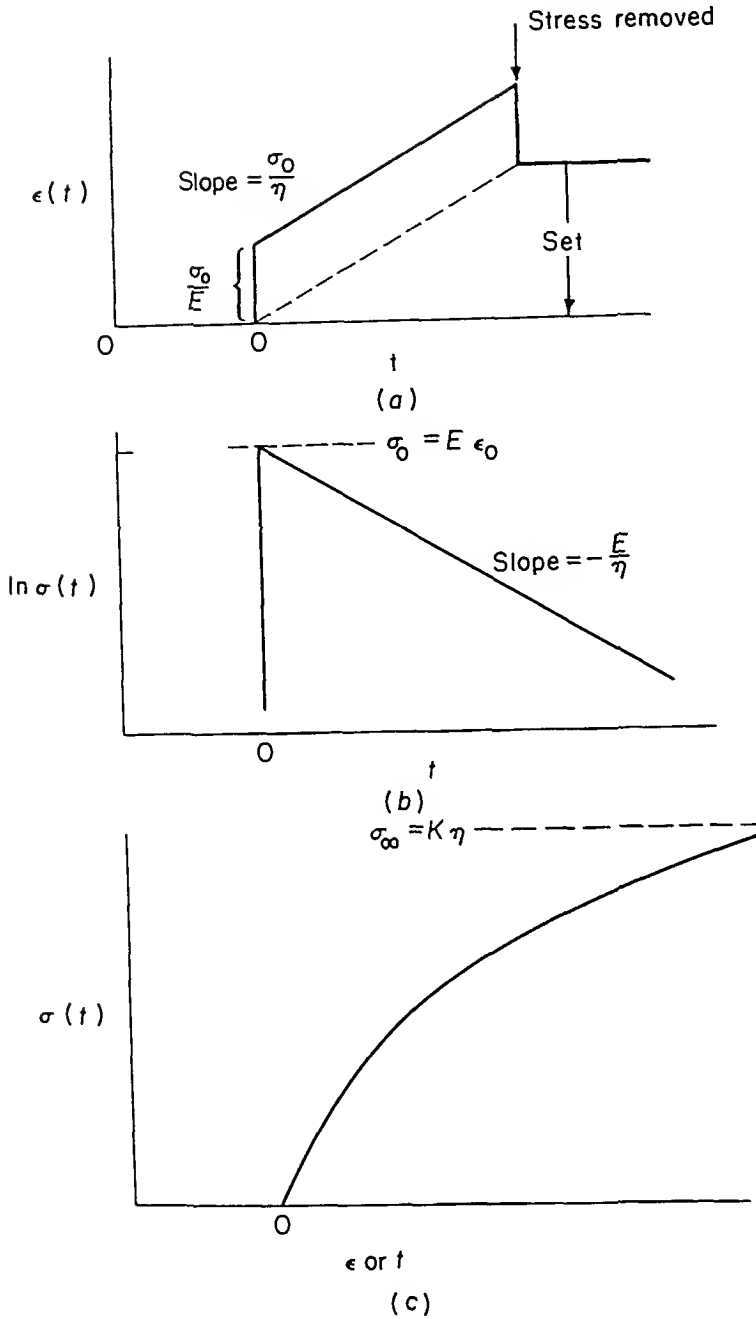


FIGURE 8-6

The Maxwell model in (a) creep, (b) stress relaxation, and (c) constant rate of extension.

deformation of the spring is recovered. The flow of the dashpot is retained as a permanent "set." A real, un-cross-linked polymer often gives this type of behavior. Another popular method of presenting experimental creep data is to plot the elongation vs. time on log-log paper. A straight line on this kind of plot gives the Nutting equation [7]

$$\log \epsilon(t) = \log A + s \log t \quad (8-31)$$

where $\log A$ and s are the intercept and slope of the plot, respectively.

Stress Relaxation

A fixed elongation ϵ_0 is applied at time $t = 0$ and held (Fig. 8-6b). We desire stress as a function of time $\sigma(t)$.

$$\frac{d\epsilon}{dt} = \frac{d\epsilon_1}{dt} + \frac{d\epsilon_2}{dt} = 0 \quad (8-32)$$

$$E^{-1} \frac{d\sigma}{dt} + \frac{\sigma}{\eta} = 0 \quad (8-33)$$

$$\int_{\sigma_0}^{\sigma(t)} \frac{d\sigma}{\sigma} = -\frac{E}{\eta} \int_0^t dt \quad (8-34)$$

$$\ln \frac{\sigma(t)}{\sigma_0} = -\frac{Et}{\eta} \quad (8-35)$$

A time-dependent modulus $E(t)$ can be defined as

$$E(t) = \frac{\sigma(t)}{\epsilon_0} = E \exp \left(-\frac{Et}{\eta} \right) \quad (8-36)$$

The term η/E , the *relaxation time*, is a measure of the rate at which stress decays. The linear viscoelastic region, of course, corresponds to $E(t)$ being independent of ϵ_0 .

Constant Rate of Strain

Many commercial testing machines operate under conditions that approximate $d\epsilon/dt = K_0$. We want stress as a function of time or of elongation, since $\epsilon = K_0 t$ (Fig. 8-6c).

$$\frac{d\epsilon_1}{dt} + \frac{d\epsilon_2}{dt} = K_0 \quad (8-37)$$

$$E^{-1} \frac{d\sigma}{dt} + \frac{\sigma}{\eta} = K_0 \quad (8-38)$$

$$\int_0^{\sigma(t)} \frac{d\sigma}{K_0 \eta - \sigma} = \frac{E}{\eta} \int_0^t dt \quad (8-39)$$

$$\sigma(t) = K_0 \eta \left[1 - \exp \left(-\frac{Et}{\eta} \right) \right] = K_0 \eta \left[1 - \exp \left(-\frac{E\epsilon}{K_0 \eta} \right) \right] \quad (8-40)$$

Harmonic Motion

If a sinusoidal force acts on a Maxwell element, the resulting strain will be sinusoidal at the same frequency, but out of phase. The same holds true if the strain is the input and the stress the output. For example, let the strain be a sinusoidal function of time with frequency ω (rad/s),

$$\epsilon = \epsilon_m \sin \omega t \quad (8-41)$$

The motion of the Maxwell element (with modulus E and relaxation time $\theta = \eta/E$) is given by

$$\frac{d\epsilon}{dt} = \frac{1}{E} \frac{d\sigma}{dt} + \frac{\sigma}{\theta E} \quad (8-42)$$

The resulting stress (see App. 2A) will be directly proportional to E . Also, the magnitude will be affected by the product $\omega\theta$ and will *lead* the strain by an angle $\delta = \cot^{-1} \omega\theta$:

$$\sigma = \epsilon_m E \frac{\omega\theta}{(1 + \omega^2\theta^2)^{1/2}} \sin(\omega t + \delta) \quad (8-43)$$

The situation is shown in Fig. 8-7. A more common notation for sinusoidal tests is the complex dynamic modulus E^* , which is made up of a dynamic modulus E' and a loss modulus E'' :

$$E^* = E' + iE'' = \frac{\sigma^*}{\epsilon^*} \quad (8-44)$$

Let the strain be a complex oscillating function of time with maximum amplitude ϵ_m and frequency ω :

$$\epsilon^* = \epsilon_m \exp(i\omega t) \quad (8-45)$$

The real strain is the real part of the complex strain ϵ^* . The resulting ratio of stress to strain can be written (App. 2B) as

$$\frac{\sigma^*}{\epsilon^*} = \frac{E\omega^2\theta^2}{1 + \omega^2\theta^2} + i \frac{\omega\theta E}{1 + \omega^2\theta^2} \quad (8-46)$$

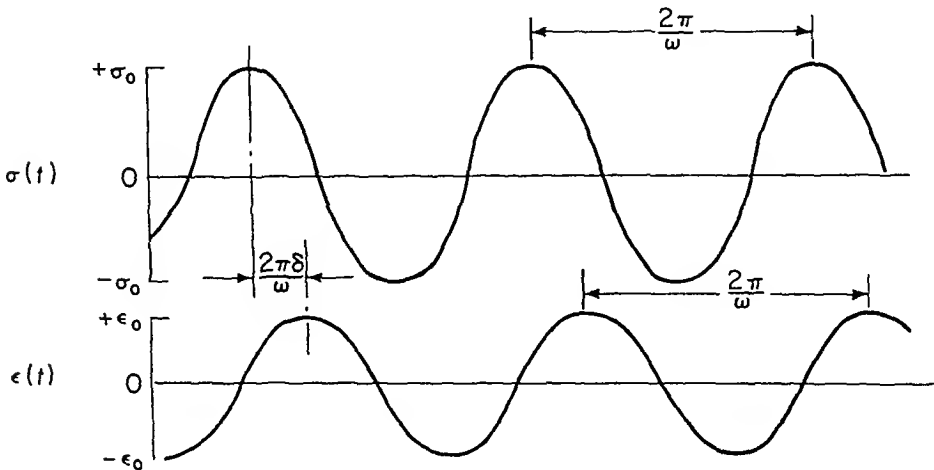


FIGURE 8-7

The Maxwell element in harmonic oscillation.

$$\text{or } \sigma^* = \sigma_m \exp(i\omega t + \delta)$$

that is, σ^* leads ϵ^* by a loss angle δ . Once again, the actual stress is the real part of the complex stress σ^* . Identification with Eq. (8-44) leads to

$$E' = \frac{E\omega^2\theta^2}{1 + \omega^2\theta^2} \quad E'' = \frac{E\omega\theta}{1 + \omega^2\theta^2} \quad (8-47)$$

$$\tan \delta = \frac{1}{\omega\theta} = \frac{E''}{E'} \quad (8-48)$$

Another term sometimes used is the dynamic tensile viscosity η'_T :

$$\eta'_T = \frac{E''}{\omega} \quad (8-49)$$

The variations of E' , E'' , and $\tan \delta$ with θ are shown in Fig. 8-8. E'' also is a measure of energy lost per cycle per unit volume (u_e), since

$$u_e = \pi E'' \epsilon_{\max}^2 \quad (8-50)$$

where $\epsilon_{\max}$ is the maximum amplitude of strain. The dissipation of energy in a cyclic process is sometimes known more familiarly as *hysteresis*.

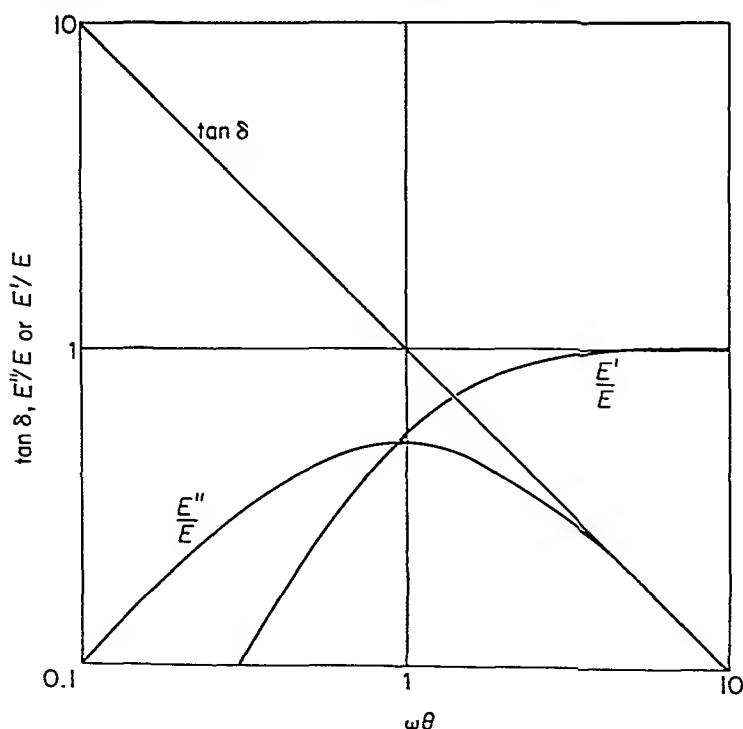
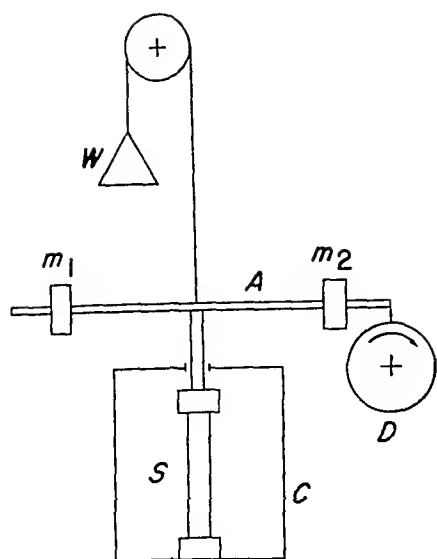


FIGURE 8-8

The quantities E' , E'' , and $\tan \delta$ as functions of E and θ for the Maxwell element.

**FIGURE 8-9**

Torsion pendulum. Sample *S* in conditioning chamber *C* acts as the restoring element. The moment arm *A* with masses m_1 and m_2 is counterbalanced by weight *W*. Amplitude of oscillation is recorded on drum *D* using thermal or light-sensitive paper.

It is noteworthy that in an oscillatory experiment we can detect a peak in loss angle or loss modulus at a transition point such as T_g or T_m (where $\omega = 1/\theta$), whereas creep, stress relaxation, and constant rate of strain give only changes in level of modulus.

8-4 DYNAMIC MEASUREMENTS

A number of commercial instruments are made that apply a harmonic stress or strain to a sample and measure the response [8, 9]. Such devices have the advantage that the cycles are repeated many times and the sample can come to a steady state. Analysis of in-phase and out-of-phase responses follows along the lines of the Maxwell model discussed in the previous section. Variations in geometry and frequency can permit the examination of many materials. A disadvantage of the technique is that the energy dissipated within the sample may cause the temperature to increase. One way to minimize the effect is to store only a small amount of energy in the sample initially and then to measure the rate of dissipation without any additional inputs of energy. This is done in stress relaxation. A dynamic mechanical analog is the pendulum. In the common pendulum a mass on the end of a string is given an initial input of energy (by raising it above its resting place). Potential energy is converted to kinetic energy as the mass returns to its rest position and again into potential energy as it rises. The frequency of oscillation of the mass is independent of amplitude.

A torsion pendulum is a particularly useful device for examining the modulus and internal friction of polymers. When the sample geometry is in the form of a cone-and-plate or concentric cylinders, the pendulum can be used for very weak gels, which are hard to characterize in conventional testing machines. Recording models are available which give a complete record of amplitude versus time. However, even manual estimation of frequency of oscillation and the number of cycles to decrease the amplitude by some factor can be quite useful.

In any torsion pendulum the sample is the energy storing and dissipating element (*S* in Fig. 8-9), and the external masses (*m*) can be used to regulate the frequency of

oscillation ω . The stiffness of the sample (torque per unit twist $\mathfrak{J}/\psi'$) depends on the shear modulus G and a geometric factor K'' . Formulas for K'' are tabulated (Table 8-2). The overall equation is

$$\frac{\mathfrak{J}}{\psi'} = GK'' = \omega^2 I \left[1 + \left(\frac{\Delta}{2\pi} \right)^2 \right] \quad (8-51)$$

The last term contains the logarithmic decrement Δ , which is the logarithm of the ratio of amplitudes A for successive cycles n :

$$\Delta = \ln \left(\frac{A_n}{A_{n+1}} \right) \quad (8-52)$$

It represents the fraction of stored energy lost per cycle. The moment of inertia of the moving part of the system usually is due mainly to external masses and can be calculated from

$$I_r = \frac{m' L^2}{12} \quad (8-53)$$

for a transverse rod of total mass m' and length L rotating about its center, and

$$I_m = mr^2 \quad (8-54)$$

for a mass m at a distance r from the center of rotation.

Example The restoring element is a piece of plasticized vinyl laboratory tubing and the formula for a thin-walled tube is used (Table 8-2). The apparatus is outlined in Fig. 8-9. $I = 7.4 \times 10^3 \text{ g}\cdot\text{cm}^2$, $L = 10 \text{ cm}$, $t = 0.15 \text{ cm}$, $D = 0.85 \text{ cm}$, and therefore, $K'' = 7.2 \times 10^{-3} \text{ cm}^3$. In Fig. 8-10, the oscillations are seen to have a period of 1.67 s corresponding to

TABLE 8-2
Geometric Factor K'' for Torque per Unit Twist

Sample geometry	Geometric factor, K''	
1. Beam in torsion	See Table 8-1	
2. Thin-wall tube: D = average diameter t = wall thickness L = length	$\left(\frac{t\pi D^3}{4L} \right)$	(8-55)
3. Sample between concentric cylinders: R_1, R_2 = radii of inner and outer cylinders L = length of sample	$\left(\frac{4\pi L}{R_1^{-2} - R_2^{-2}} \right)$	(8-56)
4. Sample between a cone and a plate: R = radius of cone ψ = angle between cone and plate	$\left(\frac{2\pi R^3}{3\psi} \right)$	(8-57)

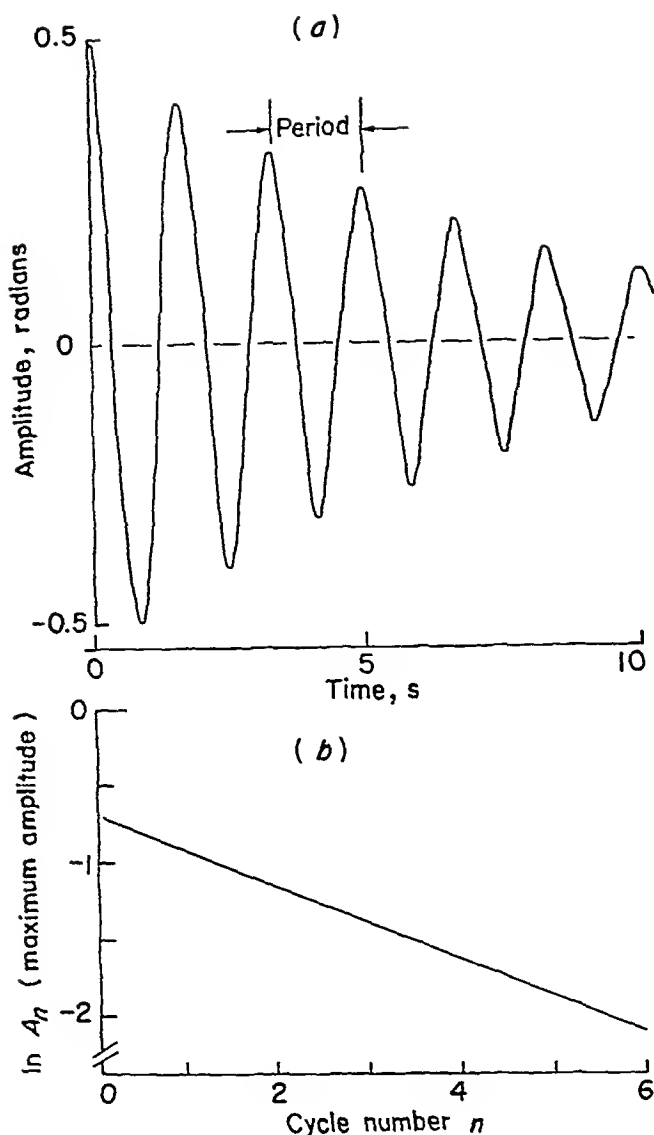


FIGURE 8-10

Typical analysis of torsion pendulum. (a) Oscillating trace made by tip of moment arm gives a period of 1.67 s corresponding to a frequency of 0.600 Hz or 1.20π rad/s. (b) Plot according to Eq. (8-52) gives a logarithmic decrement of 0.23.

$\omega = 3.77$ rad/s and $\Delta = 0.23$. Equation (8-51) then gives $G = 1.4 \times 10^7$ dyn/cm² or 1.4×10^6 Pa. A loss modulus G'' the product of G and Δ , sometimes is used. In this case, G'' is 0.32×10^6 Pa.

When oscillations are slow, as in this example, manual measurement of successive amplitudes is as simple as making marks with a pencil at the extreme position of the moment arm for each cycle. Faster oscillations require some mechanical recording device, especially when the amplitudes are very small. Figure 8-19 (Sec. 8-7) illustrates the use of the torsion pendulum for multiple transitions.

In one modification the restoring element is not simply the polymer sample, but some semirigid substrate in or on which the polymer is mounted. If blotting paper

is impregnated with polymer, the restoring element does not change in rigidity very much at transitions, but the loss peaks are quite easily detected [10]. In the “torsional braid” pendulum, a glass braid is impregnated with polymer. Because of the inert nature of the glass, the torsion pendulum will respond with changes in damping and stiffness, not only for transitions but also for chemical reactions such as oxidation, polymerization, and condensation [11, 12].

8-5 REAL POLYMERS—FIVE REGIONS OF VISCOELASTICITY

The time-dependent modulus for a typical amorphous polymer, poly(methyl methacrylate), measured by stress relaxation at various temperatures is shown in Fig. 8-11. One way to define the five regions of viscoelasticity [13] is to take a cross section of the modulus-time curve at some fixed relaxation time—say 100 h, 1 h, or 0.001 h

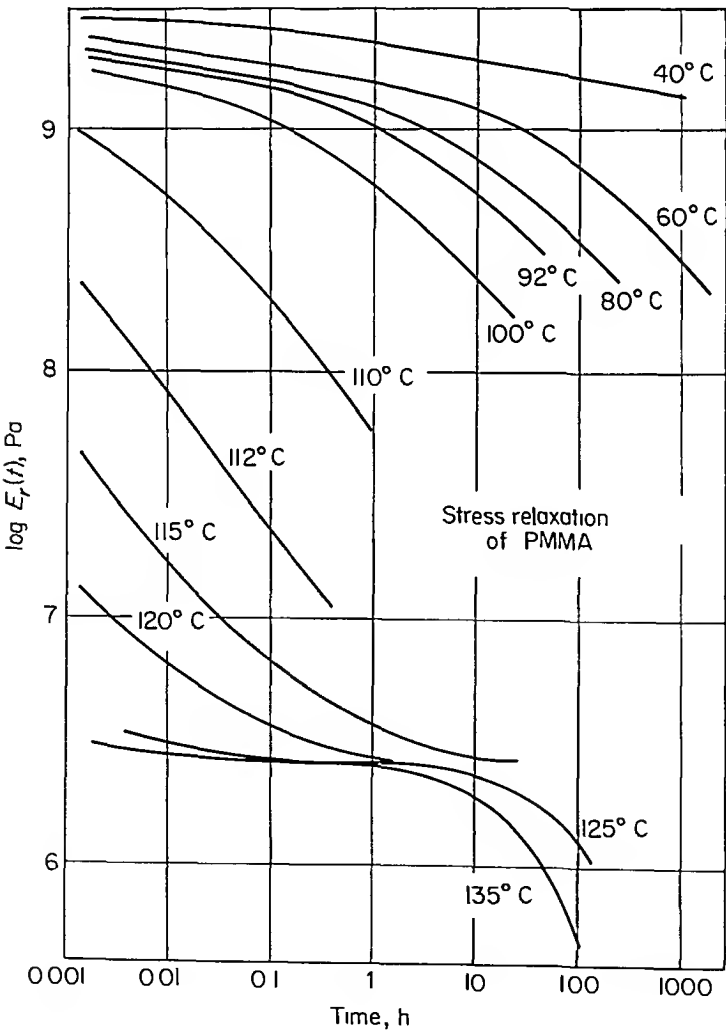


FIGURE 8-11
Log $E_r(t)$ vs. log t for unfractionated poly(methyl methacrylate) of $\bar{M}_0 = 3.6 \times 10^6$ [14].

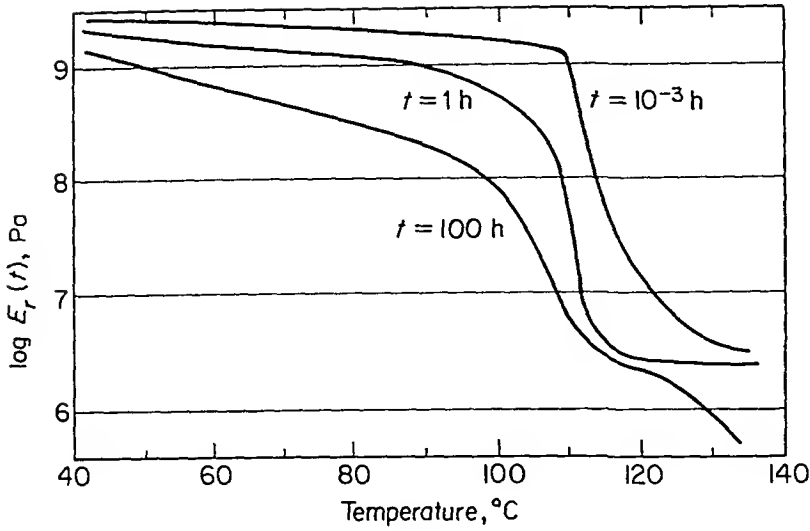


FIGURE 8-12

Modulus-temperature master curve based on cross sections of Fig. 8-9.

(Fig. 12). In each of these there are two reasonably well-defined plateaus. The first, at $E = 10^9$ or 10^{10} Pa, is the region of glassy behavior; the second is the region of rubbery behavior. Between the two plateaus we have the main *glass transition*. Figure 8-12 illustrates the rate dependence of this important temperature. Finally, at high temperatures *rubbery flow* marks the transition to the *liquid flow* region.

Horizontal shifting of stress-relaxation curves from Fig. 8-11 to correspond with that at some reference temperature T_R gives the composite curve in Fig. 8-13. This would be an academic exercise except that this time-temperature superposition is real and has been confirmed by experiments covering extremes of time scales at the same temperature. The horizontal shifts $[\log t(T) - \log t(T_R)]$ along the time axis in the vicinity of T_g are correlated by the WLF equation (7-27).

$$\log a_T = \log \frac{t(T)}{t(T_g)} = \frac{-17.44(T - T_g)}{51.6 + (T - T_g)} \quad (8-58)$$

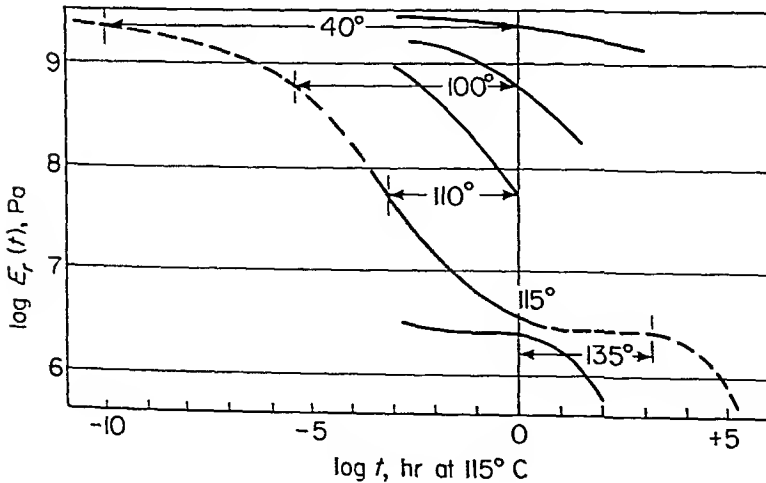


FIGURE 8-13

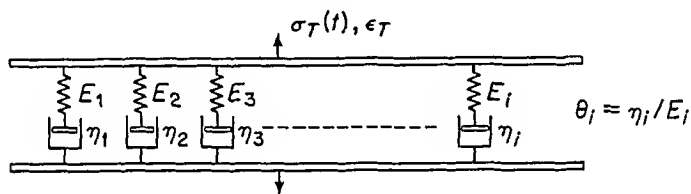
Modulus-time master curve based on time-temperature superposition of data in Fig. 8-9. Times referred to temperature of 115°C.

Obviously, the curves could be shifted to any temperature other than T_g also by the same equation ($T_R = 115^\circ\text{C}$ in Fig. 8-13, while $T_g = 105^\circ\text{C}$).

The significance of this generalization cannot be overemphasized. Again and again, we find in the literature methods of superposing time and temperature for mechanical and other properties in amorphous and partially amorphous materials. Whatever modifications are introduced usually reduce the behavior back in the direction of Eq. (8-58).

8-6 GENERALIZED MAXWELL MODEL [15]

In Fig. 8-14 we compare stress-relaxation curves for a single Maxwell element with the same glassy modulus as the "master curve" but with various values of η . Obviously, this simple model cannot approach the behavior of the real system. But suppose we used a model made up of Maxwell elements in parallel held at fixed elongation ϵ_T which is the same for all elements:



The total time-dependent force $\sigma_T(t)$ is the sum of the forces acting on the individual elements σ_i .

$$\sigma_T(t) = \sum \sigma_i = \sum \epsilon_T E_i \exp\left(-\frac{t}{\theta_i}\right) \quad (8-59)$$

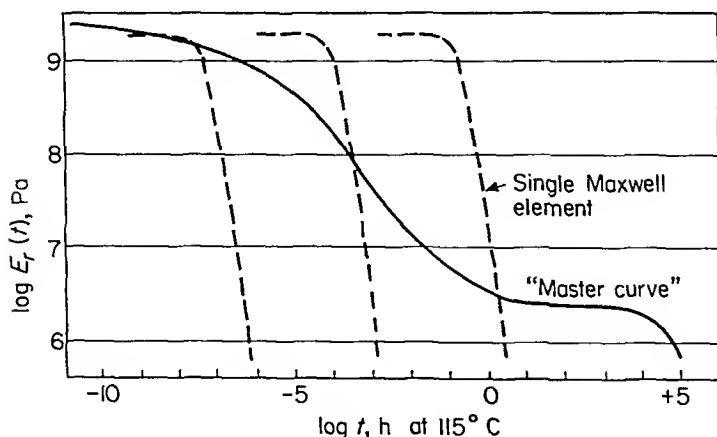


FIGURE 8-14

Master curve for poly(methyl methacrylate) compared with single Maxwell elements.

The overall time-dependent modulus $E_T(t)$ is also definable:

$$E_T(t) = \frac{\sigma_T(t)}{\epsilon_T} = \sum E_i \exp \left(-\frac{t}{\theta_i} \right) \quad (8-60)$$

The synthesis of $E_T(t)$ from known values of E_i and θ_i is simplified by the use of semilog paper.

Example Derive $E_T(t)$ for $0 < t < 200$ s when

i	E_0 , dyn/cm ² $\times 10^{-8}$	E_0 , MPa	θ , s
1	1.000	10.0	100
2	0.667	6.67	50
3	0.333	3.33	25

For each element, $E_i(t)$ is given by a straight line on semilog paper with intercept $(E_i)_0$ and a negative slope of $(\theta_i)^{-1}$ (each divided by 2.303, since we are using paper based on logarithms to the base 10) (Fig. 8-15). Adding the curves arithmetically gives $E_T(t)$ directly:

$$E_i(t) = (E_i)_0 \exp \left(-\frac{t}{\theta} \right) \quad (8-61)$$

$$E_T(t) = \sum_{i=1}^3 E_i(t) \quad (8-62)$$

Note that $E_T(t)$ is *not* a straight line in Fig. 8-15.

For an infinite number of elements, the continuous analog is

$$E_T(t) = \int_0^{\infty} E(\theta) \exp \left(-\frac{t}{\theta} \right) d\theta \quad (8-63)$$

$$\text{or } E_T(t) = \int_{-\infty}^{+\infty} \bar{H}(\log \theta) \exp \left(-\frac{t}{\theta} \right) d(\log \theta) \quad (8-64)$$

where $\bar{H}(\log \theta) = 2.303\theta E(\theta)$. Both $E(\theta)$ and $\bar{H}(\log \theta)$ are called the distribution of relaxation times. A number of mathematical models have been proposed for the relationship between $\bar{H}$ and θ . When these are inserted in Eq. (8-64), the infinite array is reduced to something represented by a few parameters. Two elementary models are the box and the wedge:

Box:

$$\bar{H} = E_m \quad \theta_3 < \theta < \theta_m \quad \text{and} \quad \bar{H} = 0 \quad \text{for } \theta < \theta_3 \text{ or } \theta > \theta_m \quad (8-65)$$

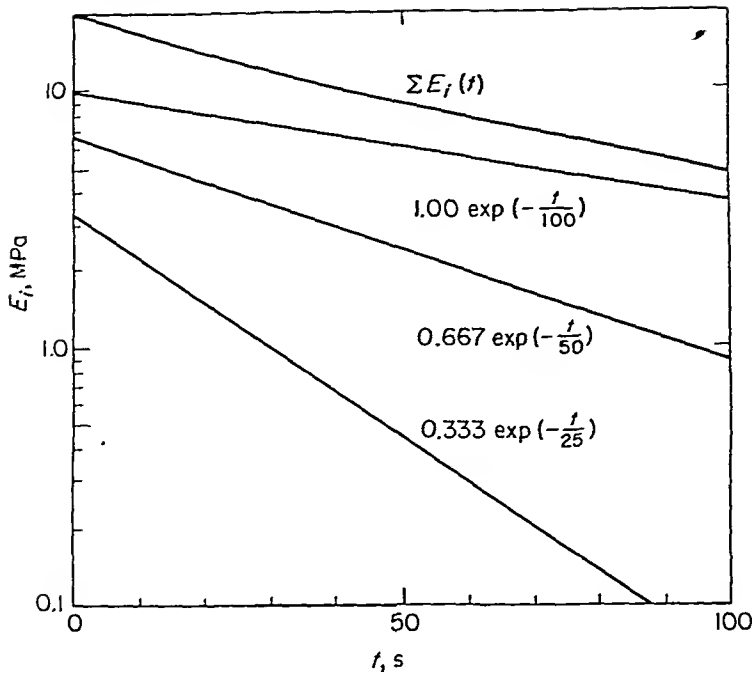


FIGURE 8-15

Time-dependent modulus for individual Maxwell elements and for the sum of three elements in parallel $\Sigma E_i(t)$.

Wedge:

$$\bar{H} = \frac{M_0}{(\theta)^{1/2}} \cdot \theta_1 < \theta < \theta_2 \quad \text{and} \quad \bar{H} = 0 \quad \text{for } \theta < \theta_1 \text{ or } \theta > \theta_2 \quad (8-66)$$

The functions that result when these distributions are inserted into Eq. (8-64) are the incomplete gamma function (for the wedge) and the exponential integral function (for the box), each evaluated between limits of θ (Fig. 8-16). A comparison of $E_T(t)$ for

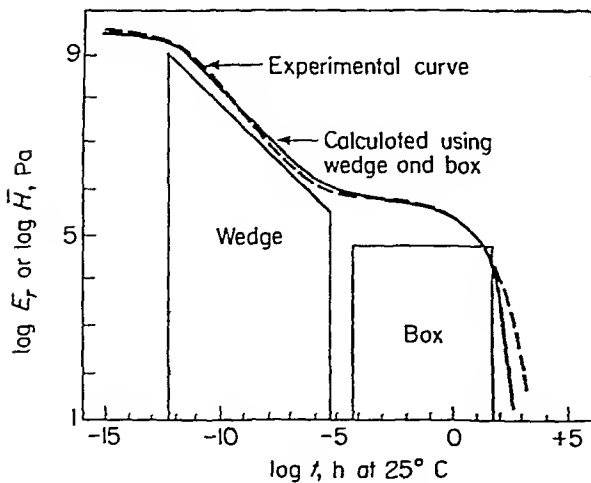


FIGURE 8-16

Master curve for polyisobutylene as determined by superposition of experimental stress-relaxation data (dashed line) and from the insertion of the wedge and box models in Eq. (8-57) [15].

polyisobutylene with the fit based on a box and a wedge shows the degree of approximation of the wedge to the glass-transition region and the box to the rubbery flow region (Fig. 8-16).

8-7 EFFECT OF MOLECULAR WEIGHT

As long as the molecular weight exceeds that of a polymer segment, glassy behavior and T_g should be relatively insensitive to further increases in molecular weight. For our purposes here, this can be taken as 50 to 100 chain atoms, although there is no clear-cut definition of a segment for all situations. However, rubbery behavior, according to Eq. (8-23), depends on the chain density N in moles per unit volume. In fact, as α approaches unity,

$$E = \frac{d\sigma}{d\epsilon} = \frac{d\sigma}{d\alpha} = 3kTN \quad (8-67)$$

Therefore, we expect E to increase linearly with absolute temperature and with cross-link density for network polymers. In Fig. 8-17, lines corresponding to various cross-link densities are shown. The effect of T on E is corrected in the ordinate (T_R is any reference temperature). Very high cross-link densities preserve pseudo-glassy behavior to high temperatures. A thermoset such as a phenol-formaldehyde resin remains glassy with no measurable mechanical transition in the absence of chemical change. But a network polymer has an infinite molecular weight. For a finite molecular weight, the cross-links are temporary ones and are due to entanglements or to the time needed for segments to diffuse by one another. The effect of molecular weight on the curves also is shown (Fig. 8-17). At a low enough molecular weight, there is no rubbery plateau and the glass goes directly to a melt.

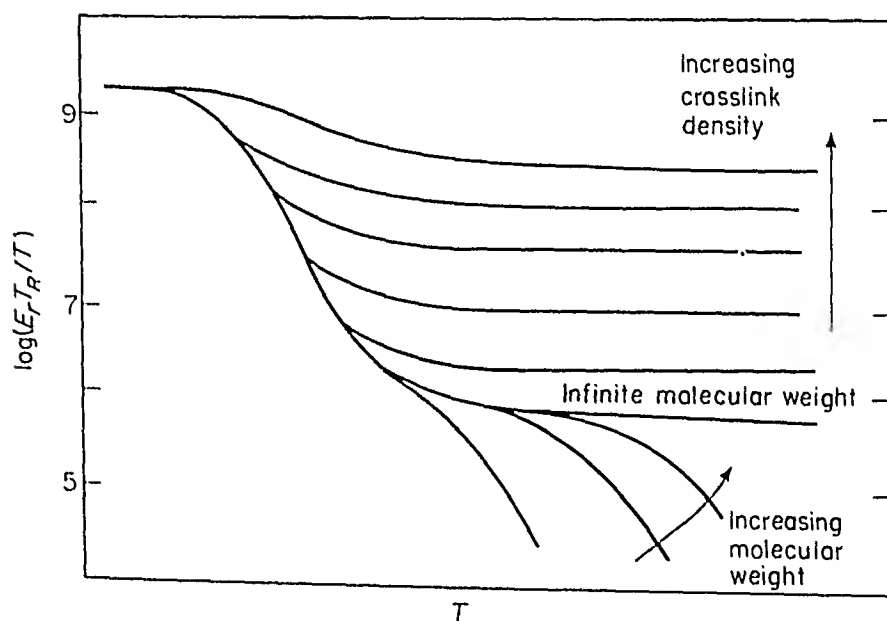


FIGURE 8-17

Qualitative effects of increasing molecular weight and cross-linking on the master curve.

8-8 EFFECT OF CRYSTALLINITY

The main response of a partially crystalline material to an external stress is borne by the amorphous fraction. In materials of low crystallinity, say, less than 30% crystallinity, the crystallites function as temperature-dependent cross-links. We expect the glassy and rubbery plateaus to exist as before, but we expect the rubbery region to undergo a time-independent, fairly sharp transition at the melting temperature T_m . Of course, smaller crystallites and those formed at lower temperatures have lower T_m 's than others. This blurs the transition.

With highly crystalline materials, the glass transition may become less pronounced. The behavior of nylon 66 is illustrative (Fig. 8-18). The glass transition is quite sensitive to moisture but involves a modulus change of only about tenfold compared with a thousandfold for a completely amorphous material (Fig. 8-13). However, both above and below T_g there is a continuous loss in stiffness due to decrease in crystalline content.

When an oscillating stress is imposed on the material, the fraction of energy dissipated per cycle (logarithmic decrement) is a sensitive measure of transitions. The data for partially crystalline tetrafluoroethylene (Fig. 8-19) show four transitions below the melting temperature, which is about 600 K. At 176 K the transition is thought to be the hindered rotation of small segments of the polymer chains. The transition of 292 K marks changes in crystalline morphology from triclinic to disordered hexagonal and a change in the helical repeating unit of 13 to 15 chain atoms. At 303 K there is further disordering of the hexagonal lattice to an irregular repeating unit. At 400 K we have the main glass transition T_g .

8-9 EFFECT OF FILLERS

In the region of small deformations, fillers have much the same role as crystallites, especially if the filler surface is wetted by the polymer. The behavior of carbon black in a cross-linked natural rubber is typified by Fig. 8-20 showing an increase in stiffness (spring constant) with loading and a moderate increase in damping, i.e., fractional energy loss per cycle. Note that the stiffness increases with temperature in accordance with Eq. (8-23) when no filler is added. The situation is more complex when filler is present. The modulus of a glassy polymer is increased by fillers, and T_g may be increased somewhat also (Fig. 8-21).

8-10 OTHER TRANSITIONS

There are other transitions in molecular conformations that give rise to loss peaks in oscillatory experiments such as the torsion pendulum. Often the modulus changes by such a small amount at a minor transition that performance properties are not noticeably affected. It has been pointed out that an additional amorphous change occurs well below the main glass transition temperature of poly(tetrafluoroethylene) (Fig. 8-19). In some literature the main T_g is designated as the α transition, and transitions at successively lower temperatures are termed β and γ . For nylon 66, loss peaks identified with the amorphous region are seen at 200 K (β transition) and at 135 K

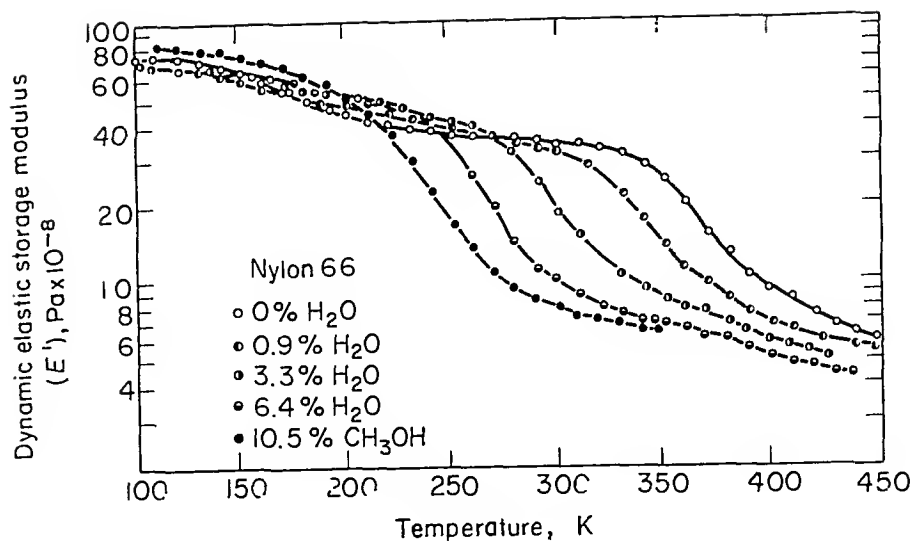


FIGURE 8-18

Dynamic modulus vs. temperature for nylon 66 containing various amounts of water or methanol [16].

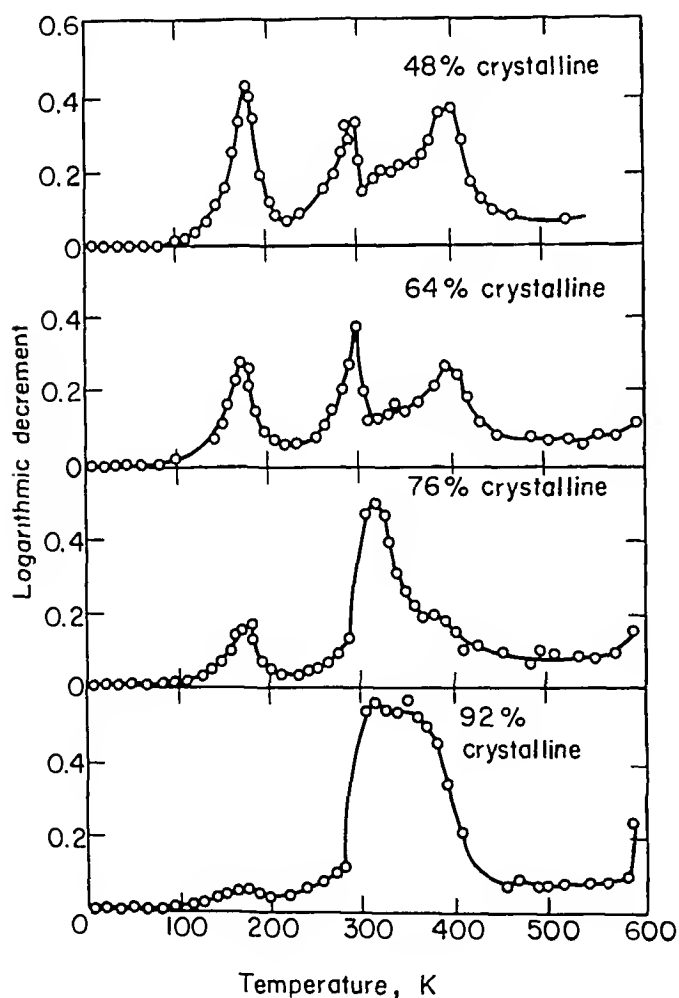


FIGURE 8-19

Variation with temperature of the logarithmic decrement for samples of poly(tetrafluoroethylene) of various degrees of crystallinity [17].

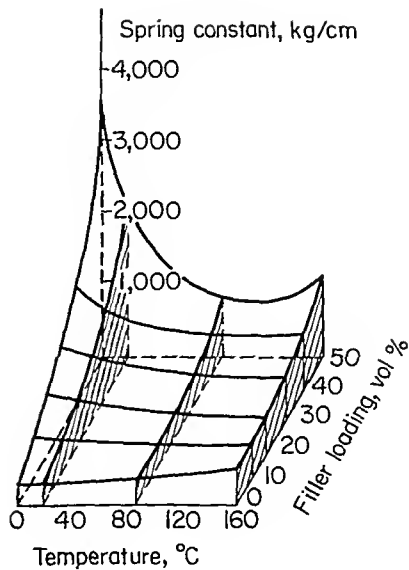
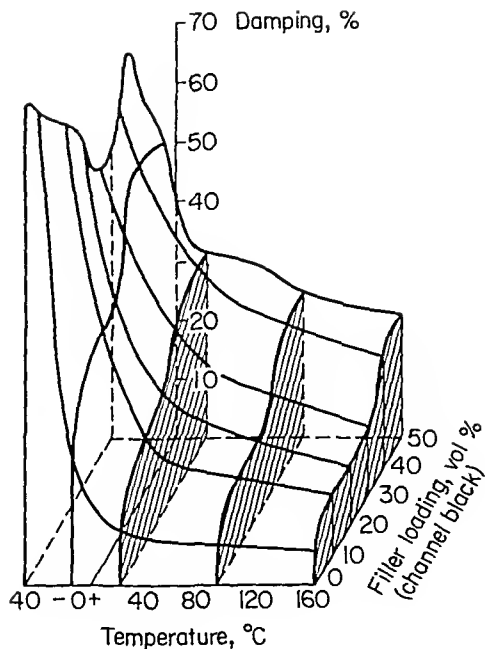


FIGURE 8-20

Contour representation of dependence of dynamic properties on filler loading and temperature (after Ecker [18]).

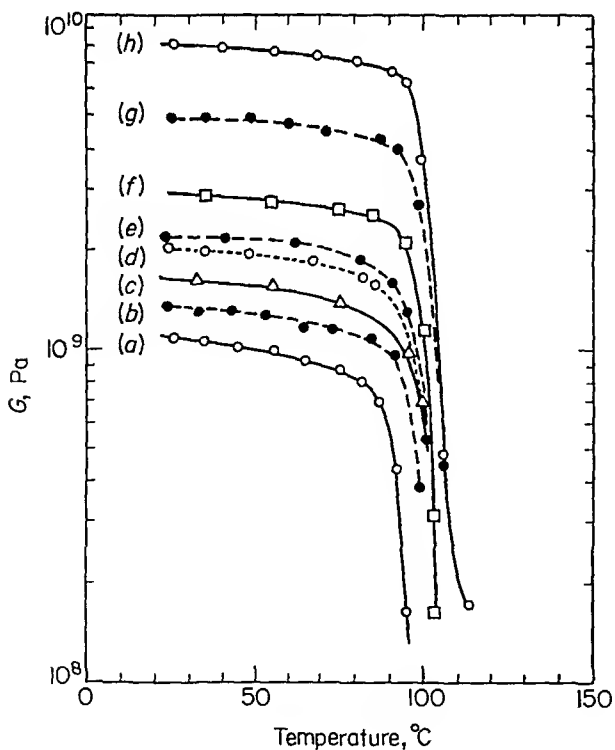


FIGURE 8-21

Shear modulus vs. temperature for (a) polystyrene and for polystyrene containing (b) 20% calcium carbonate, (c) 20% asbestos, (d) 20% mica, (e) 40% asbestos, (f) 60% asbestos, (g) 40% mica, and (h) 60% mica [19].

(γ transition) [20]. The storage modulus (Fig. 8-18) scarcely changes at those temperatures.

Much more controversial is the observation of a loss peak above T_g in the amorphous melt. This $T_{1,1}$ transition temperature represents a change from one liquid state to another [21, 22]. For polystyrene $T_{1,1}$ is about 70°C higher than T_g ; and for polyisobutylene it is about 105°C higher than the T_g measured by the same method.

PROBLEMS

- 8-1. An unstressed rubber band becomes longer when heated. A stretched rubber band with constant load becomes shorter when heated. Is this behavior consistent with Eq. (8-23)? Explain.
- 8-2. An ideal rubber is stretched to 1.10 times its unstretched length at 27°C (300 K) supporting a stress of 150 psi. After aging 10 days in air at 127°C , the stress at 1.10 times its unstretched length is only 100 psi (at 127°C). If the original polymer contained 0.015 mol of cross-links per unit volume originally, how many moles of cross-links per unit volume were lost or gained on aging?
- 8-3. The following data are obtained on a sample of natural rubber. Calculate the stress to be expected at 100% elongation for the dry rubber (in Pa) at 27°C .

Swelling in benzene at 27°C :

$$\chi = 0.44$$

$$v_2 = 0.20$$

$$V_1 = 100 \text{ cm}^3/\text{mol}$$

$$R = 8.31 \text{ J/mol}\cdot\text{K}$$

- 8-4. An ideal rubber has a nonlinear stress-strain curve. If a 1.00 cm cube of such a rubber is compressed to 0.98 cm by a mass of 3 kg, what stress is going to be required to stretch a 5 cm strip of the same rubber to a length of 7.5 cm?
- 8-5. An ideal rubber band is stretched to a length of 15.0 cm from its original length of 6.00 cm. It is found that the stress at this length increases by an increment of $1.5 \times 10^5 \text{ Pa}$ when the temperature is raised 5°C (from 27° up to 32°). What modulus ($E = \sigma/\epsilon$) should we expect to measure at 1% elongation at 27°C ? Neglect any changes in volume with temperature.
- 8-6. How much work (J) is done on an ideal rubber band that is slowly and reversibly stretched to $\alpha = 2$? The initial slope of the stress-strain curve is 2 MPa and the volume of the rubber band is 4.0 cm^3 .
- 8-7. A polymer can be represented by two Maxwell elements connected in parallel, each with the same spring modulus. In a stress relaxation experiment the stress decreases to 23.7% of its initial value after 10 min. If the relaxation time of the first element is 10 min, what is the relaxation time of the second element?
- 8-8. A certain polymer sample can be represented by a single Maxwell element. When a tensile stress of 10^3 Pa is applied for 10 s, the maximum length attained by the sample is 1.15 times the original length. After removal of the stress (at 10 s), the length is only 1.10 times the original length. What is the relaxation time of the element?

8-9. A cross-linked polymer can be represented by three Maxwell elements in parallel with constants:

$$E_1 = E_2 = E_3 = 10^5 \text{ Pa}$$
$$\theta_1 = 10 \text{ s} \quad \theta_2 = 100 \text{ s} \quad \theta_3 = \text{infinity}$$

- (a) What stress is required for a sudden ($t = 0$) elongation to twice the original length?
- (b) What will be the stress after 100 s at twice the original length?
- (c) What will be the stress after 10^5 s at twice the original length?
- 8-10. Assume that a polymer can be approximated by three Maxwell elements in parallel each having the same modulus but with viscosities for elements 1, 2, and 3 having the relationship

$$\eta_1 = 4\eta_2 = 9\eta_3$$

- Plot $\log (\sigma / \sigma_0)$ vs. t / θ_1 and vs. $\log t / \theta_1$ for the overall assembly between $t / \theta_1 = 0.01$ and $t / \theta_1 = 2$, where θ_1 is the relaxation time for element 1. What is the relaxation time [t for $\ln (\sigma / \sigma_0) = -1$] for the assembly?
- 8-11. At times such that $t \ll \theta_1$, a polymer has a glassy modulus of E_g . At times greater than $t = \theta_2$, it exhibits liquid flow. Between θ_1 and θ_2 , the transition can be described by a continuous distribution of relaxation times, $E(\theta) = Y / \theta^2$. Derive an equation for the time-dependent modulus $E(t)$ as a function of t , Y , θ_1 , and θ_2 . Also, express E_g in terms of Y , θ_1 , and θ_2 . Plot the curve of $\log E(t)$ vs $\log t$ from $t = 0.01$ to $t = 100$ s for the following set of constants: $E_g = 10^9$ Pa; $\theta_1 = 0.1$ s; $\theta_2 = 10$ s. How does the result compare with the relaxation of a single Maxwell element?
- 8-12. The Voigt (or Kelvin) element resembles the Maxwell element except that the spring and dashpot are in parallel rather than in series. Show that the creep compliance of such an element is

$$J(t) = (E)^{-1} \left[1 - \exp \left(-\frac{tE}{\eta} \right) \right]$$

- 8-13. For 4 Voigt elements (see Prob. 8-12) in series for a creep experiment, plot compliance vs. time on log-log paper for each element and add them to get the total compliance. What constants do you obtain for a Nutting equation fitted between the times $t = 10$ and $t = 1000$ s?

	Element number			
	1	2	3	4
E_i , Pa	0	1.0×10^4	1.333×10^4	2.0×10^4
η_i , Pa·s	2.0×10^6	5.0×10^5	1.333×10^5	4.0×10^4

- 8-14. An amorphous polymer in a creep experiment behaves like a Maxwell element joined in series with a Voigt element. A constant load of 10^4 Pa is applied to

a tensile specimen at time $t = 0$. After 10 h the strain is 0.05 cm/cm. The load is removed. The strain can be described *thereafter* by

$$\text{Strain} = \frac{3 + e^{-t'}}{100} \quad \text{where } t' = t - 10 \text{ (h)}$$

Identify and evaluate the four model parameters. Use proper units.

- 8-15. An ideal rubber has a density of 0.93 g/cm^3 and an average molecular weight between cross-links of 1250 g/mol . It is placed in a torsion pendulum (rectangular specimen) and cooled to 100 K , which is 80°C below the glass transition temperature. In the pendulum it exhibits a frequency of 55 cycles/s . What frequency do we expect to observe at 27°C ? Assume that changes in dimensions of the sample are negligible between the extremes of temperature. In the glassy state it resembles room-temperature polystyrene, that is, a shear modulus of 3.0 GPa .
- 8-16. Samples of a given amorphous polymer are strained 1% at a variety of temperatures. Draw a typical diagram for stress (measured after 10 s) vs. temperature for the polymer. Identify on the diagram (a) T_g and (b) the rubbery plateau. How would the diagram be changed if:
- (c) The material were degraded to 10% of the original molecular weight?
 - (d) The material were loosely cross-linked?
 - (e) The diagram were plotted using stress measured after 10 h?
- 8-17. In a certain test a constant stress is instantly applied to a dumbbell sample (in tension). Three materials are tested. A rubber reacts by deforming rather rapidly to start and then more and more slowly until it reaches an equilibrium extension. A thermoplast reacts by deforming almost instantly to some substantial extension and then deforming further linearly with time. A thermoset reacts by deforming almost instantly to an equilibrium extension.
- (a) Describe the behavior of each material with an appropriate combination of dashpots and springs.
 - (b) Describe what happens to each model when the stress is instantaneously removed.
- 8-18. How much of a shift in T_d (temperature at peak in mechanical loss) do you expect from the WLF equation when the time scale of the test is decreased by a factor of 10?
- 8-19. Creep data for a sample of plasticized poly(vinyl chloride) at six temperatures can be represented by the Nutting equation with constants as follows: $J(t) = A't^n$ and $10 \text{ s} < t < 1000 \text{ s}$.

Temperature $T, ^\circ\text{C}$	A' s^n/Pa	n
37	9.5×10^{-10}	0.08
44	1.3×10^{-9}	0.19
50	1.3×10^{-9}	0.68
53	2.2×10^{-8}	0.37
63	2.2×10^{-7}	0.18
72	5.2×10^{-7}	0.10

Assuming $T_g = 50^\circ\text{C}$, construct a plot of $J(t)$ vs $\log t$ at 50°C over the range of t from 10^{-3} to 10^7 s by choosing shift factors according to the WLF equation. If a sample has a strain of 0.0005 units after 5 s of creep at constant stress at 50°C , how long will it take (in seconds) to grow to a strain of 0.050 unit?

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9

ULTIMATE PROPERTIES

9-1 FAILURE TESTS

Most industrial tests of polymer systems are carried to failure with some degree of simulation between test and end use. A manufacturer of plastic cups is more interested in a fast breaking test that simulates dropping a cup than in slow, steady deformation. The compromise that is reached is between a specific test (dropping a cup, wearing out a tire on the road, parachuting greater weights until the cords on the chute break) and a more general one (impact strength, sandpaper abrasion, high-speed tensile strength).

Usually, the *ultimate strength* of a material is the stress at or near failure. For most materials, failure is catastrophic with a complete break. However, some materials, especially spherulitic crystalline polymers, reach a point where a large inelastic deformation starts (*yielding*) but continue to deform and absorb energy long beyond that point. Even when strength is defined unequivocally and measured with care and statistical confidence, it can be a misleading criterion for the unwary designer. Although it is one of the most widely specified parameters, tensile strength is almost never the limiting factor in a practical application. Seldom, if ever, is a polymer subjected in an end use to a single, steady deformation in the absence of aggressive environments or stress concentrators. In garments, rugs, instrument cases, tires, book covers, and upholstery, polymers fail from repeated stresses, from impact, from penetration by sharp objects, or by propagation of a tear. It is only insofar as the tensile strength correlates with toughness, tear resistance, and fatigue strength that it has real merit.

Toughness can be defined as the energy absorbed at failure. The area under the stress-strain curve has the units of joules per cubic meter when stress is in pascals and strain is in meters per meter. If stress is in pounds per square inch and strain is expressed as inches per inch, the area under the curve has the units of inch-pounds per cubic inch, which also represents energy per unit volume. The energy may be stored

elastically as in unfilled rubber, or it may be dissipated as heat as in the permanent deformation of a crystalline material. A rod made from a glass with a strength of 100 MPa can be used to suspend 10 times the weight that a rubber rod with a strength of 10 MPa can withstand. But because the rubber may have an elongation at break that is a thousand times larger than that of the glass, the energy that the rubber rod can absorb before breaking may be many times that of the glass rod.

There is an important qualitative difference between the mechanical properties at small deformations and those at large. The modulus, for example, truly is a *material property*. On the other hand, most ultimate properties are *sample properties*. Failure invariably takes place at a defect or stress concentrator. Every value reported must be regarded as an average that represents a distribution. A typical frequency function found useful for rubber testing is the double exponential [1], which can be represented in integral form by

$$\sigma_b(n) = \bar{\sigma}_b + s \ln \left(-\ln \frac{n-0.5}{N} \right) \quad (9-1)$$

where $\sigma_b(n)$ is the strength of the n th sample when all N samples of a population are ranked in order of decreasing strength. The mode of the distribution is $\bar{\sigma}_b$, and the standard deviation is s . An analysis of 24 tests shows values for tensile strength that vary from 25 to 29 MPa (3500 to 4100 psi) (Fig. 9-1). All points are equally valid, since all are part of the expected distribution. If the twenty-fourth point had a tensile strength of 20 MPa (3000 psi), one would be justified in discarding it as being atypical of the distribution. In making plots for this purpose, one arranges the samples in order of decreasing tensile strength.

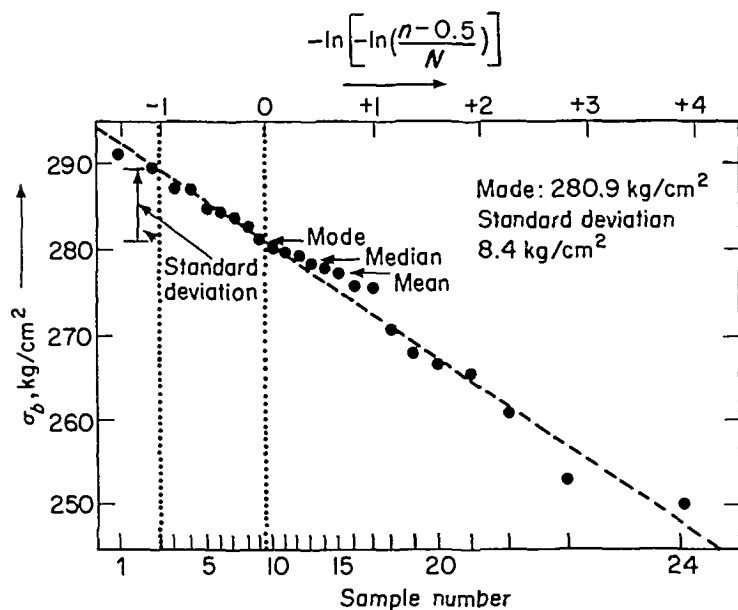


FIGURE 9-1

Stress at break plotted according to Eq. (9-1). All points are typical [1].

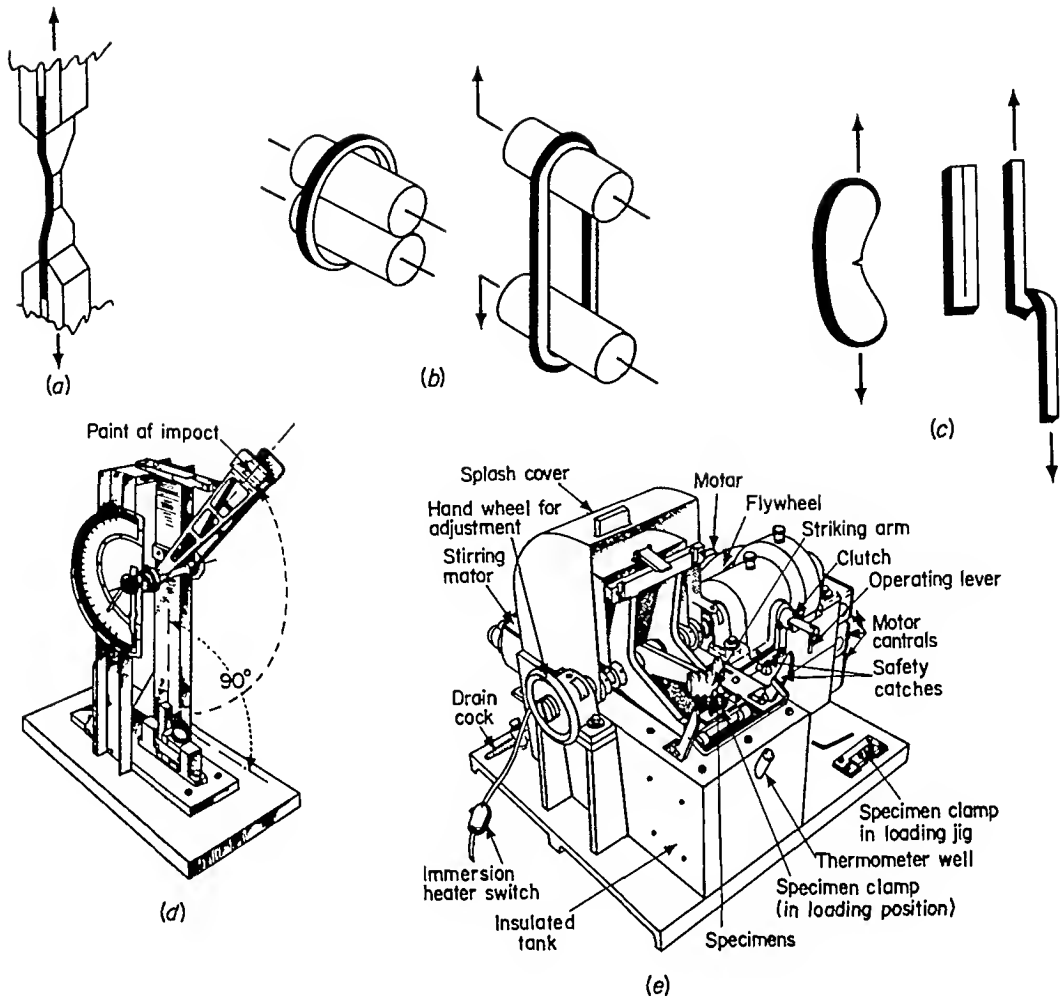


FIGURE 9-2

Mechanical failure tests. (a) Tensile test on dumbbell specimen; (b) tensile test on ring specimen; (c) notched crescent and trousers tear specimens; (d) Izod impact test machine [2], and (e) motor-driven brittleness temperature tester [2].

9-2 CONSTANT-RATE-OF-STRAIN TESTS

A common tensile test involves elongating a dumbbell-shaped sample held in jaws that separate at a constant rate (Fig. 9-2). The stress is measured as a function of time. Because the section of uniform cross section of the sample does not elongate at a constant rate, an independent measure of elongation is required if a stress-strain curve is to be constructed from the experiment. The true rate of extension in the center portion can be estimated by measuring with a ruler the separation of two *bench marks* that were originally a convenient distance apart, say 1 in. At each half-inch or inch interval, a pip may be placed on the record of stress to indicate increments of strain. An *extensometer* (extension-measuring device) for materials that elongate between 2 to 10 times before breaking can be a pair of clamps that are connected by a tape. As the clamps separate, the tape moves with one and is pulled through the other. If the tape has a pattern that generates a signal at equal intervals, pips can be put on the stress record automatically. When the extension at break is very small, as with glassy

materials, an elaborate means of monitoring extension is to follow and record the position of several luminescent bench marks by means of photocells and a servomotor. Despite the difficulty of measuring strain accurately, the dumbbell samples have the great advantage that ultimate failure will take place in the center of the sample and will not be affected by stress concentration at the jaws.

Molded, die-cut, or lathe-cut rings can be used for rubbery samples. The rate of strain is uniform, so that the stress-time record is also a stress-strain record. With care the strength measured on ring samples is the same as that on dumbbells. However, stress concentration at the holder is difficult to avoid even when the holder is lubricated or rotated. Also, the initial portion of the stress-strain curve may be distorted because the stress needed to deform the ring into an oval may mask the stress due to uniform elongation.

Tests with fibers offer another complication. With the uniform cross section, any local yielding or necking is likely to start at the holders and the effective length of the sample may be increased by "jaw penetration." Long samples or multiple samples wound around spools at either end will minimize the uncertainty in length.

Anyone who has tried to open a cellophane-wrapped article has a real appreciation for the difference between the stress needed to rupture a smooth-edged film and the stress needed to propagate a tear. An ordinary piece of cellophane tape with a cross section of a thousandth of a square inch will support a load of many pounds. The slightest notch with a razor on one edge will reduce the supportable load to several ounces. Although there are a number of tear-testing geometries to choose from, the *trousers tear test* has the merit that the stress to propagate the tear often stays at a constant value, making it easier to estimate than some others where the tear propagates so rapidly that only a peak stress can be read (Figs. 9-2 and 9-3).

We have pointed out that the extension at break for a glassy sample often is so small that it becomes hard to measure. In a flexural test, the elongation occurs on one side of the sample and compression on the other. A small elongation at break corresponds to a large flexural deflection, which is easily measured. The simple beam with sliding supports is used most often.

For an adhesive bond, the peel strength (normal to the bonded surface) or the shear strength (in the plane of the bonded surface) may be measured. For another application, the stress supportable in compression before yielding may be the most important parameter. This would be true for a rigid foam, for example.

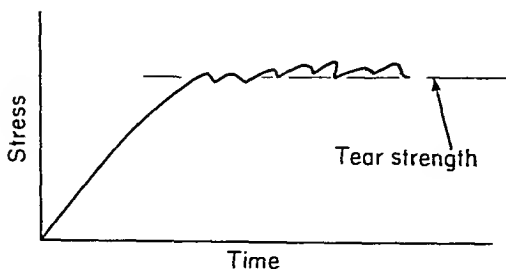


FIGURE 9-3

Typical trousers tear test diagram.

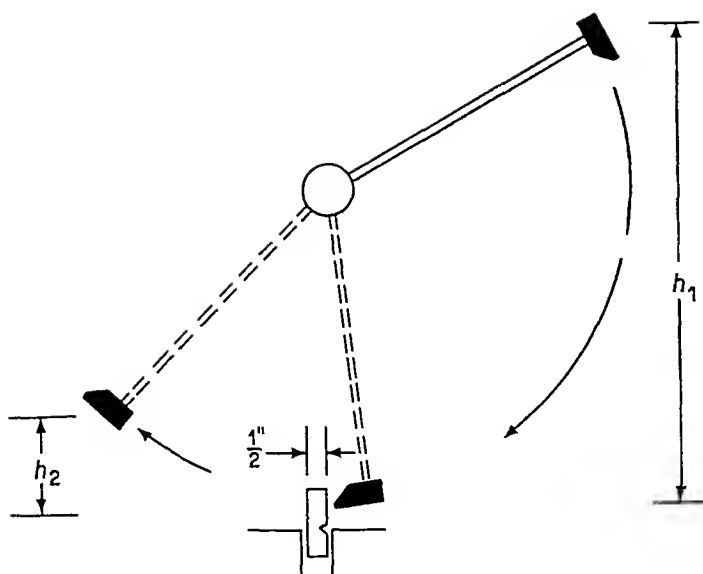


FIGURE 9-4

Impact testing (notched Izod). Original and final heights h_1 and h_2 of hammer determine strength of sample of thickness d held in vise.

9-3 BREAKING ENERGY

If more than enough energy is applied to rupture the sample, we can measure directly the total *energy to cause rupture*, or *toughness*, which is the area under the stress-strain curve. One such simple device is the impact tester, where a hammer has a certain potential energy before and after breaking the sample in flexure or tension. The energy used in breaking the sample is proportional to the difference in height before and after.

Impact strength = energy to break sample per unit thickness

$$= (h_1 - h_2) \frac{W}{d} \text{ ft} \cdot \text{lb/in} \quad (9-2)$$

Although most impact test machines in use today are calibrated in the older units of ft·lb/in, it is possible to express the results in the SI units of joules for energy and meters for width. One ft·lb/in equals 53.4 J/m.

The Izod test (Figs. 9-2 and 9-4) uses a cantilever beam, while the Charpy test uses a simple beam. Since the notch and the width of the sample are specified, the energy is usually given per unit of notched thickness. In practice, to account for friction in the apparatus, h_0 is used rather than h_1 ; h_0 is the final height with no sample. Also, some energy goes into accelerating the broken piece of sample. This can be subtracted from the impact strength, but usually it is not. The impact strength of a bar sample is measured only on glassy or crystalline materials, since most rubbers will not fracture in this test.

A pendulum arm is used to break rubber and soft plastics in the “brittleness temperature” test (Fig. 9-2). The energy to break is not measured, but the temperature is progressively lowered until the samples do fracture. The brittleness temperature so established often corresponds to T_g or T_m .

9-4 CREEP FAILURE

A single *creep test* in tension or flexure gives information on long-term dimensional stability of a load-bearing element. When combined with a variable temperature, the test measures the *deflection temperature*, where creep rate changes rapidly. Once again, this is close to T_g . The load at which deflection took place also must be specified. A more specific test holds the sample in pipe form under fixed pressure until rupture occurs. Conducted in an aggressive environment such as soapy water or organic solvents, we get a type of *environmental-stress cracking*. Although such tests are useful in predicting the service life of a product, they are even more useful when run at different temperatures and then combined by time-temperature superposition (Sec. 9-6) in order to estimate service life at some constant temperature.

9-5 FATIGUE

Most materials subjected to a stress repeatedly will fail even when that stress is well below the ultimate stress measured in a single deformation to the point of failure. When a stress is applied in an alternating fashion, as in a flexing test, the sample usually fails after a certain number of cycles. The lower the applied stress, the more cycles needed to cause failure. For some materials, the stress reaches a limit below which failure does not occur in a measurable number of cycles. Poly(tetrafluoroethylene) and poly(methyl methacrylate) in Fig. 9-5 exhibit such an *endurance limit* or *fatigue strength*, whereas nylon 6 does not. Rigid plastics such as the crystalline and glassy thermoplastics fail catastrophically, often with a sharp increase in temperature at the time of failing. A rubber being *flex-tested* may fail more gradually by the development of cracks or by the growth of a cut artificially introduced before testing. Also, in a rubber, the temperature rise due to mechanical hysteresis may be great enough to accelerate oxidative degradation.

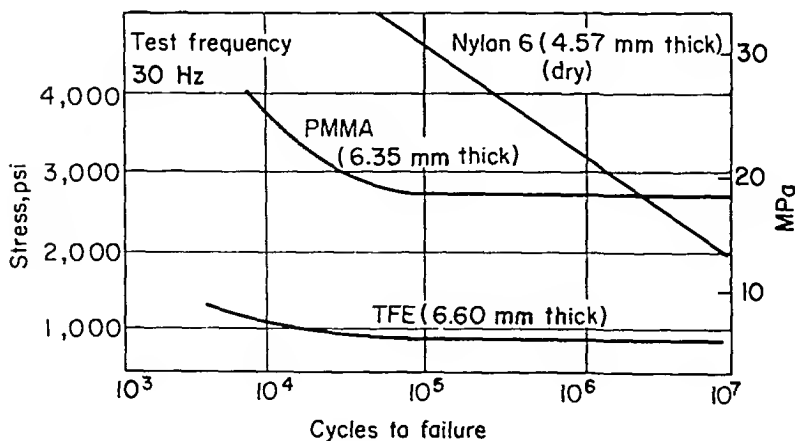


FIGURE 9-5

Fatigue life curves for nylon 6, poly(methyl methacrylate) (PMMA), and poly(tetrafluoroethylene) (TFE) [3].

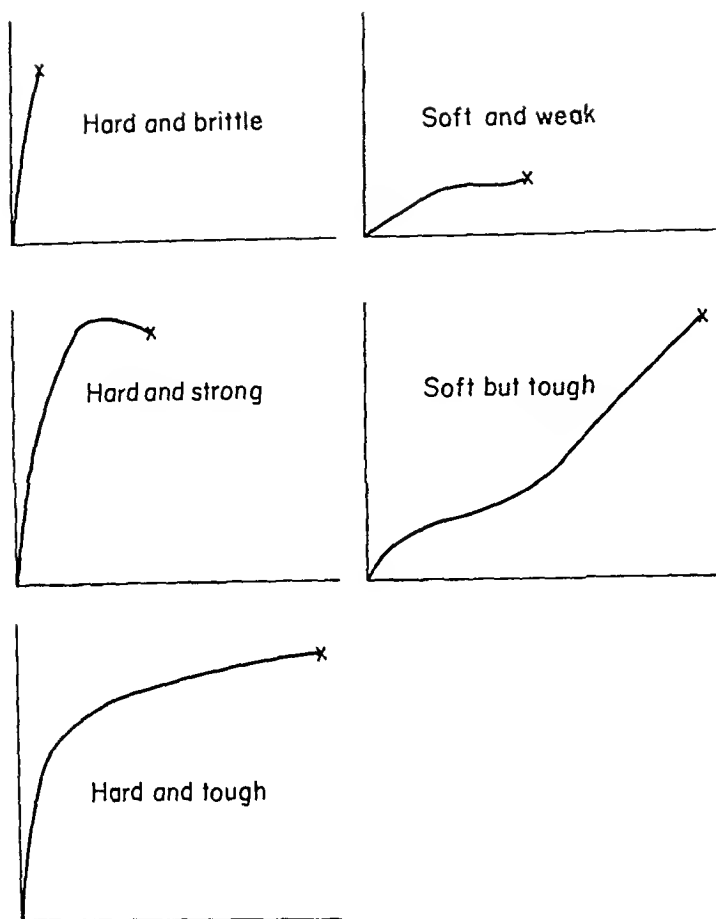


FIGURE 9-6
Types of stress-strain curves [4].

9-6 REDUCED-VARIABLE FAILURE CORRELATIONS

The relationship between stress and strain at large values of strain follows the same pattern discussed in the preceding chapter. We expect glasses and highly cross-linked networks to be brittle, rubbers to have high elongations before breaking, and crystalline materials to be strong and tough if oriented and to “neck” and yield if not oriented. However, all of these types of behavior depend on the time scale of the test, the temperature at which it is run, the presence of fillers or other polymers, and even sample geometry and history. In general [4]:

- A soft and weak material will have a low modulus, a low yield stress, and a moderate to high elongation at the break point (Fig. 9-6).
- A hard and brittle material will have a high modulus and a low elongation at break. It may not yield before breaking.
- A soft but tough material has a low modulus but a high elongation and high stress at break. It may have a low yield stress.
- The hard, strong material has high modulus, high yield stress, and high breaking stress and perhaps a moderate elongation at break.
- The hard, tough material has a high modulus, high elongation, and high stress at break.

Any amorphous polymer that is stretched undergoes some orientation of polymer segments. In this oriented state, crystallization may occur, which will increase the effective number of cross-links (see Sec. 3-4). If crystallization does not occur, the behavior of the sample to rupture may be described by the same equation as small deformations. Figure 9-7 shows that the stress-strain curves for some elastic fibers correlate well (give a linear plot) with Eq. (8-25) up to the rupture point (about 600% elongation). The most often used mechanical test is one that measures stress at constant strain rate. The ultimate tensile stress and strain at rupture varies with temperature and rate of strain. For a cross-linked unfilled rubber, which does not crystallize on stretching, the shift factors of the WLF equation (9-3) (see below) allow a reasonable superposition over a wide range of conditions. In Fig. 9-8, the stress at break σ_b is multiplied by the ratio of a reference temperature ($T_s = 263$ K) to the test temperature in accordance with the theory of rubber elasticity (Sec. 8-2). The shift factors a_T used to multiply the rate of extension R (meters per meter per second) are given approximately by the WLF equation in modified form, since T_s is not T_g (Fig. 9-9):

$$\log a_T = -\frac{8.86(T - T_s)}{101.6 + T - T_s} \quad (9-3)$$

A similar reduced curve can be produced for the elongation at break ϵ_b (Fig. 9-10). The same shift factors have been used here. The curves of stress and strain at break

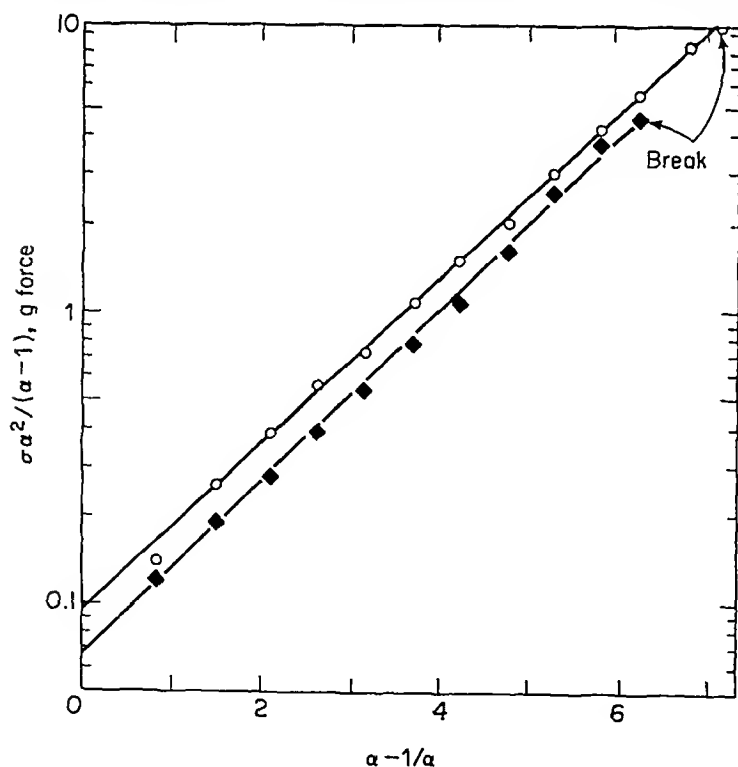


FIGURE 9-7

Stress-strain data to break for two spandex fibers plotted according to Eq. (8-25) [5].

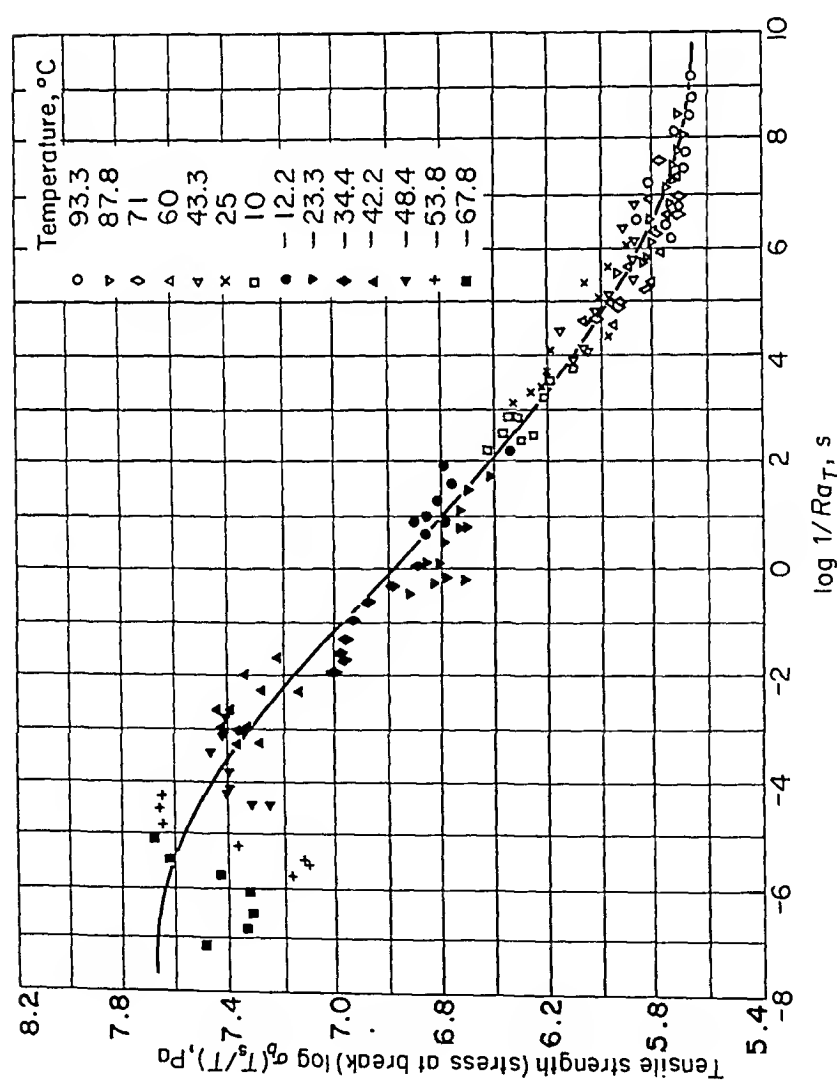


FIGURE 9-8
Variation of the tensile strength for a cross-linked styrene-butadiene rubber with reduced strain rate Ra_T . Reference temperature is 263 K [6].

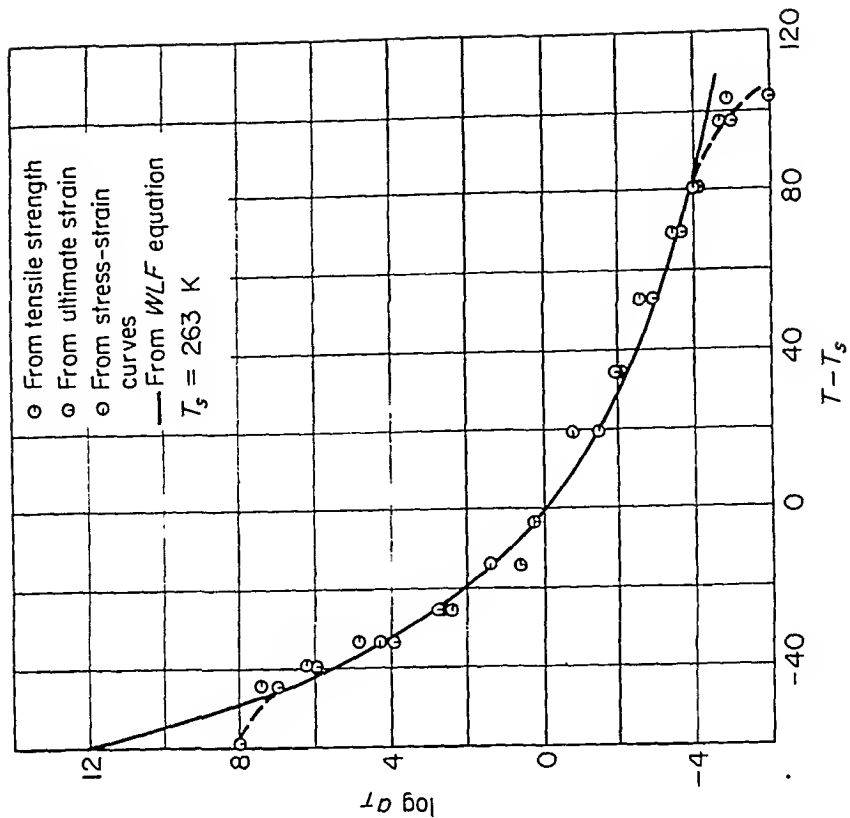


FIGURE 9-9
Experimental values of shift factor a_T from experiment and from WLF-type equation in which the reference temperature is 263 K, not T_g [6].

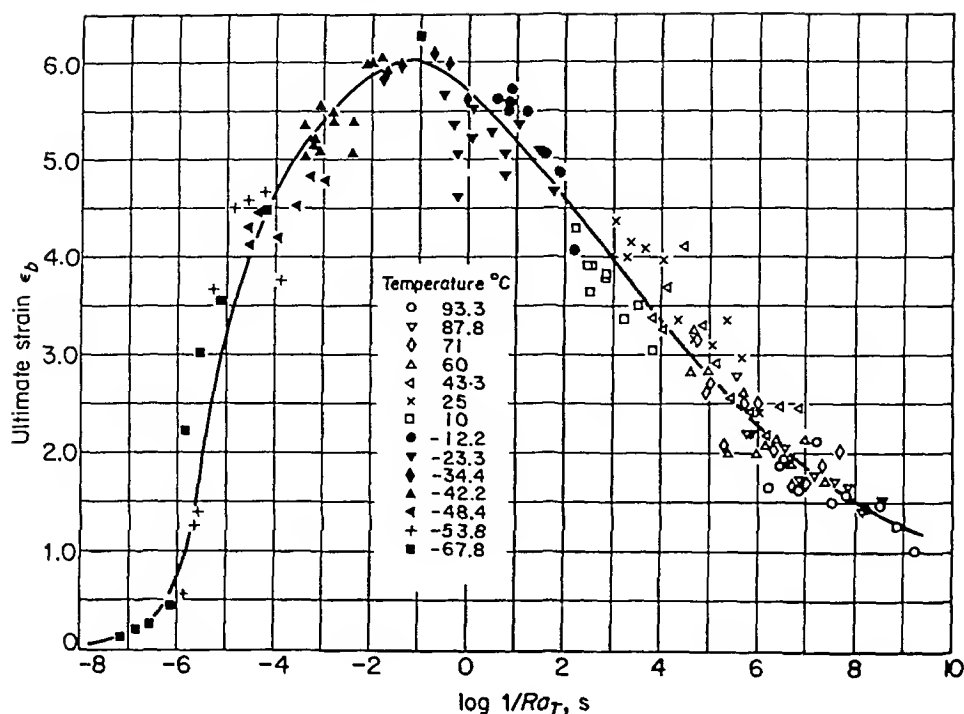


FIGURE 9-10

Variation in the strain at break for same sample as Fig. 9-8 with reduced strain rate Ra_T [6].

taken together can be used to construct a *failure envelope* in which we have eliminated the parameters of time and temperature. This general relationship is shown schematically in Fig. 9-11. Lines OA , OB , and OC are typical for constant-rate-of-strain experiments at decreasing temperatures or increasing strain rates, respectively. In the case of strain rates at constant temperature, we can superpose a time grid on the diagram, since each strain on each line corresponds to a value of elapsed time.

This is illustrated in Fig. 9-12, where the dotted lines indicate test times (isochronal lines) that increase from a to g . The lowest line, OA , is the *equilibrium* elastic line for a cross-linked material. Its position is subject to the cross-link density and temperature but independent of time. All the constant-rate-of-strain lines exhibit higher stresses at the same strain, because part of the stress is used to dissipate viscous energy in the sample. Several other cases are illustrated in Fig. 9-11. For example, let us stretch a sample from O to point D and then hold it at constant stress. This becomes a creep experiment. By following the isochronal lines, we can depict the time-dependent strain that culminates when the point F on the equilibrium curve is reached. If at point D , we held the strain constant, we would have a stress-relaxation experiment culminating in point E . On the other hand, if we extended the sample to point G and held it at constant stress or strain, the diagram predicts eventual failure. Experimental curves showing the stress relaxation culminating in failure for a synthetic rubber are shown in Fig. 9-13.

Actual failure envelopes for five cross-linked rubbery polymers are summarized in Fig. 9-14. The ordinate is the product of stress σ_b and strain ϵ_b at break, while the

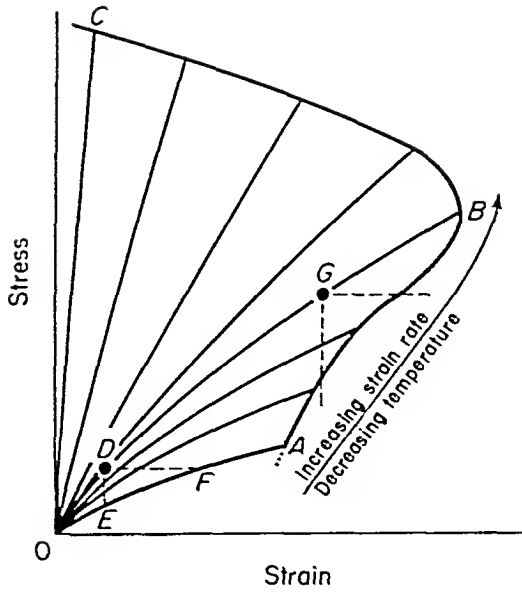


FIGURE 9-11

Schematic representation of failure envelope enclosing curves at constant strain rate. Dotted lines illustrate stress relaxation and creep under different conditions [6].

abscissa is the strain multiplied by the equilibrium modulus E_e . This allows superposition for samples varying in cross-link density. At low strains, the slope is unity, which corresponds to

$$\sigma_b = E_e \left(\frac{\epsilon_b}{\epsilon_b + 1} \right) \quad (9-4)$$

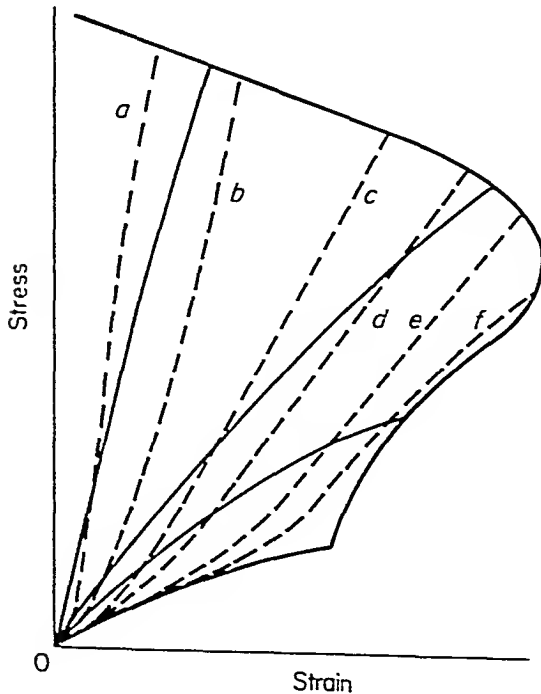


FIGURE 9-12

Isochronal lines in a hypothetical failure envelope (time increases from a through f).

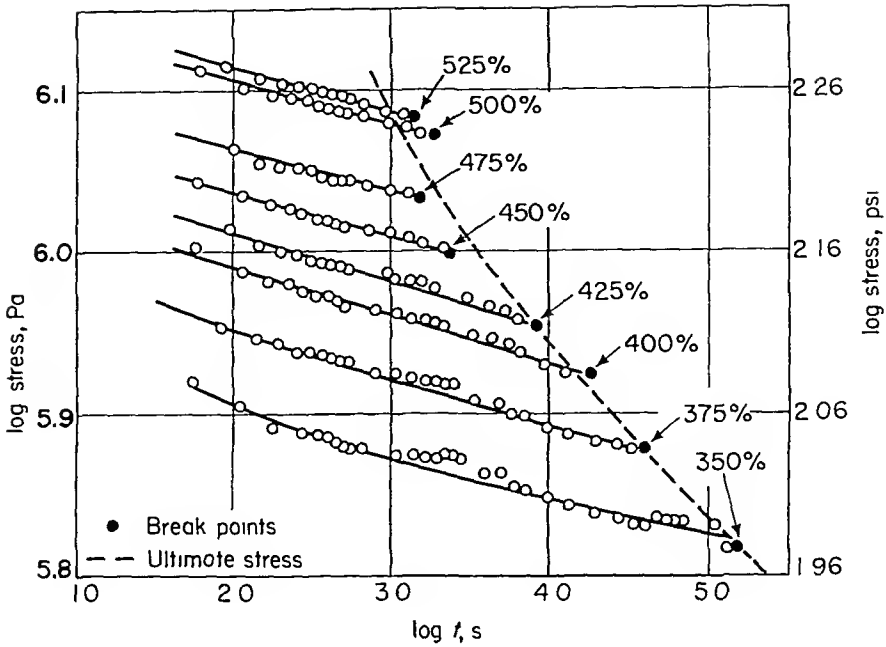


FIGURE 9-13

Stress relaxation of a cross-linked styrene-butadiene rubber at 1.7°C at elongations from 350 to 525%. Solid points indicate rupture [7].

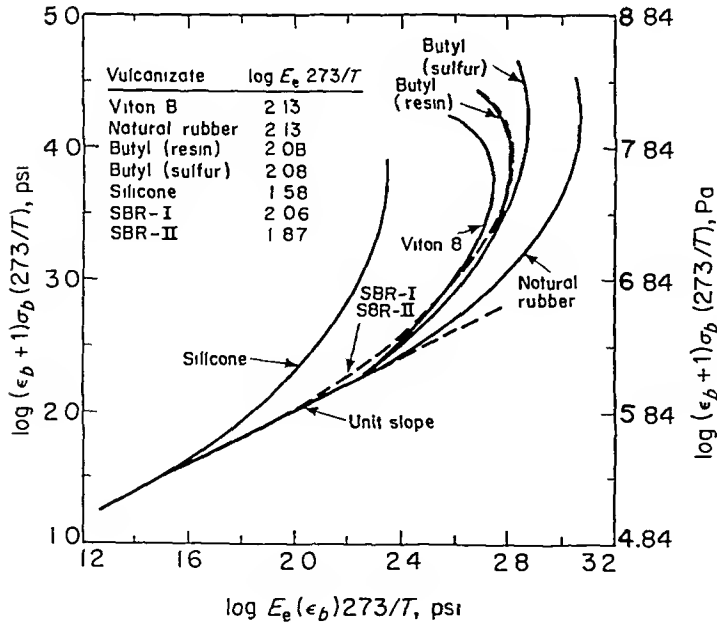


FIGURE 9-14

Failure envelopes for vulcanizates of five different polymers [7].

In general, the behavior of Eq. (9-4) is closer to that of Eq. (8-25) than that of Eq. (8-23). Curves for all the polymers in Fig. 9-14 are similar in shape. Natural rubber is not completely described, because at high elongations and lower temperatures it does crystallize. In Fig. 9-15 we show schematically the behavior of such crystallizable polymers. There is a characteristic increase in slope at high elongations because of the self-reinforcing nature of the oriented crystallites.

9-7 FRACTURE OF GLASSY POLYMERS

There are two major mechanisms by which glassy polymers yield in response to stress. Shear deformation is a localized phenomenon that may appear as shear bands. When a polystyrene cube is uniaxially compressed, the bands appear at a large angle (about 38°) to the compression direction. The bands can be about $1\text{ }\mu\text{m}$ thick and are made up of oriented polymer.

A second mechanism is crazing. Crazes are typically seen in a tensile test on a thin sample. What appear to be fine cracks at right angles to the applied stress are not cracks but crazes, "narrow zones of highly deformed and voided polymer" [8]. The typical craze contains from 20 to 90% voids and the rest fibrils oriented in the direction of the applied stress. The shear bands, in contrast, have very little void volume. Unlike actual cracks, both crazes and shear bands are capable of supporting stresses because of the oriented polymer involved. The failure of a glassy polymer in tension may involve both mechanisms [8-12].

When a crack propagates, a plastically deformed zone usually precedes the crack (Fig. 9-16). To quote Kambour [10], "Optimists concentrate on plastic deformation in crazes as a source of toughness or stress relief in polymers, while pessimists focus on crazing as the beginning of brittle fracture." The surfaces left on the crack retain a layer of craze material. The dimensions of a craze that has not yet developed into a crack are shown in the profile obtained for a craze in a thin film of polystyrene (Fig. 9-17). The total length of this craze was $189\text{ }\mu\text{m}$. The individual fibrils connecting the two sides were about 15 nm in diameter [13]. Fibrils are an essential

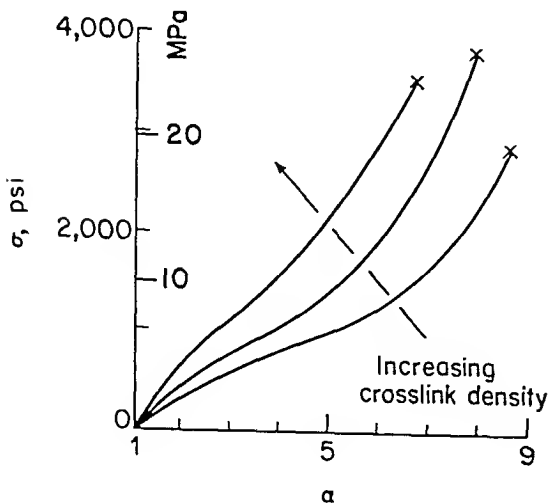


FIGURE 9-15

Typical stress-strain curves for a rubber that crystallizes at high elongations.

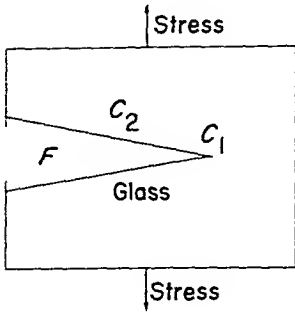


FIGURE 9-16
In response to a stress the unoriented glassy polymer is pulled into fibrils at the craze tip C_1 . At the crack tip C_2 the fibrils rupture leaving a layer (typically about 500 nm thick) of craze material on the fracture surface F .

feature of crazes. The energy absorbed in their orientation process contributes to polymer toughness.

If crack propagation is carried out in the presence of a liquid that can act as a plasticizer, the stress needed to cause crazing may be decreased by the greater ability of the polymer to be oriented as fibrils [9, 13, 14]. *Environmental stress cracking* of polymers is studied as a practical test of performance for pipes and other load-bearing applications where the polymer will be exposed to an aggressive environment. The effects are seen not only in glassy polymers, but also in semicrystalline materials such as polyethylene.

To quantify the processes occurring when a crack propagates, a model system is an elliptical hole of length $2c$ in a large sheet of material (Fig. 9-18). The stress at fracture σ_f should be related to the modulus of the material E (since E represents energy storage capability) and to the energy γ to create the new surface area in the crack. Another approach relates the strain energy released per unit area of crack growth. When the *strain energy release rate* g exceeds 2γ , fracture will result. For the model system, the latter approach gives

$$g_{Ic}^2 = \frac{\sigma_f^2 \pi c}{E} \tag{9-5}$$

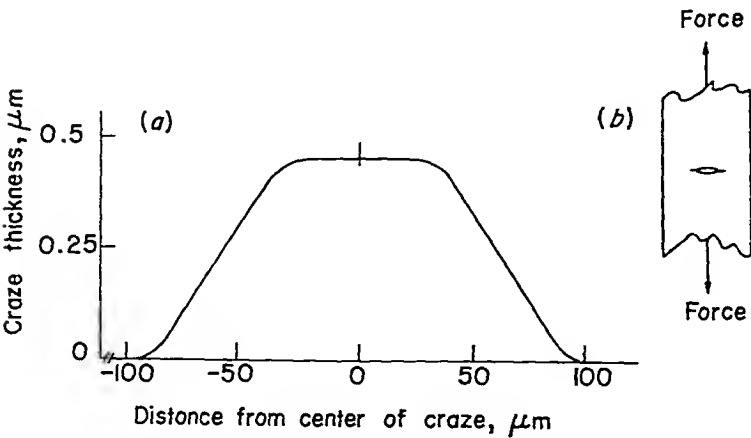


FIGURE 9-17
(a) Thickness profile for an isomated air craze in a thin polystyrene film [13]. (b) Thickness is measured in the direction of the applied force and is a measure of fibril length in the craze.

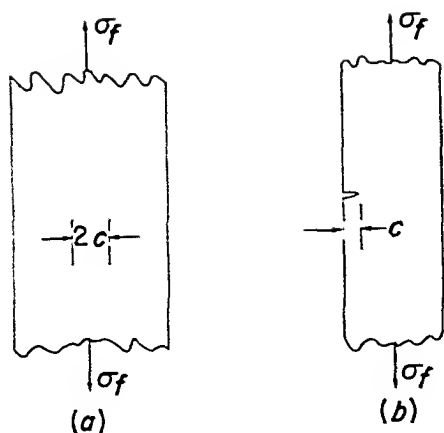


FIGURE 9-18

(a) A model system for crack propagation is an elliptical hole of length $2c$ in a large sheet of material subjected to a tensile stress σ_f . (b) It is often convenient to introduce the crack as a notch in a single edge of a sheet.

Unfortunately, various groups who study brittle fracture of polymers throughout the world choose to express their results in different ways. A related parameter used by some to describe the dependence of stress at fracture on crack size is the *critical stress intensity factor* K_{Ic} :

$$K_{Ic}^2 = 2E\gamma = S_{Ic}E \quad (9-6)$$

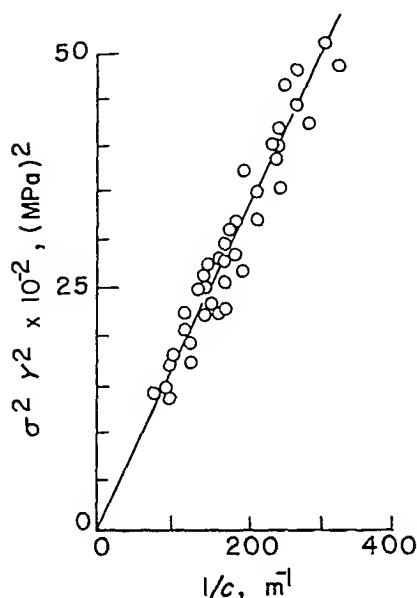
Some authors refer to K_{Ic} as the *fracture toughness*.

In an experiment corresponding to Fig. 9-18b, the specific geometry is accommodated in a constant Y , so that:

$$\sigma_f^2 Y^2 = \frac{K_{Ic}^2}{c} \quad (9-7)$$

Values of Y are tabulated for many geometries [11, 15]. For the sample of polycarbonate (Fig. 9-19), the value of K_{Ic} is $4.0 \text{ MPa}\cdot\text{m}^{1/2}$ with little dependence on the manner in which the notch was introduced or on the rate of crack propagation (within limits). For many glassy materials, including polystyrene and poly(methyl methacrylate), K_{Ic} is relatively independent of thickness. The failure process in polycarbonate is somewhat more complex. In a thin sheet the plate surfaces can contract laterally and the plastic zone extends from one surface to the other. In a thick sheet lateral contraction is constrained and part of the crack tip is put in triaxial tension, greatly reducing the overall stress needed for failure. Sheets of polycarbonate less than 3 mm thick may have a K_{Ic} of about $5.5 \text{ MPa}\cdot\text{m}^{1/2}$. The sample of Fig. 9-18 was about 5 mm thick. Very thick sheets approach a K_{Ic} of about $2.2 \text{ MPa}\cdot\text{m}^{1/2}$. The two extreme values reflect the two different failure mechanisms that predominate at the extremes in thickness.

From the standpoint of convenience, the impact “strength” (Sec. 9-3) is the most often reported measure of toughness for brittle materials. The equipment is

**FIGURE 9-19**

Brittle fracture data for polycarbonate. Points were obtained at various rates of crack growth and various forms of crack initiation [11].

inexpensive, the test is fast, and the results for notched samples of specified dimensions are satisfactorily reproducible. On the other hand, even in a notched sample much energy is used in initiating the actual crack, and the propagation energy is not clearly distinguishable.

Fracture toughness (and impact strength) is increased by various inclusions. Rigid fibers or particles that adhere well to the glassy polymer matrix can spread the applied force over a larger zone, thus decreasing local stress concentration. Inclusion of amorphous particles above their T_g increases energy dissipation by viscous deformation. Cross-linking a glassy polymer inhibits the orientation processes and usually decreases impact strength. In a typical thermoset glass such as a phenolic resin, cross-linking contributes high temperature stability. Fiber or particulate reinforcement is used to keep up the impact strength. Heterophase systems (see next section) are commonly employed when toughness is a major criterion.

Despite what has been said about the obvious differences in fracture mechanisms for glasses and rubbers, some generalizations remain. For example, the stress at failure is linear in the logarithm of time to fail (Fig. 9-20) for virtually all materials when one ignores minor variations [16].

9-8 HETEROPHASE SYSTEMS

Partly crystalline polymers will vary in stress-strain behavior depending on rate and temperature. Some three-dimensional representations for commercial polyethylene (Figs. 9-21 and 9-22) show the behavior of yield point and elongation with test conditions. Yielding often coincides with the onset of *necking* (Sec. 3-3) and marks the limit of rubbery behavior in the amorphous portion and bond bending and stretching in the crystalline portion that can be borne before spherulites become unstable (Fig. 9-23). Once a crystalline polymer is oriented, as in typical drawn fibers, the ultimate elongations are much lower. The ultimate tensile strengths are higher mainly because

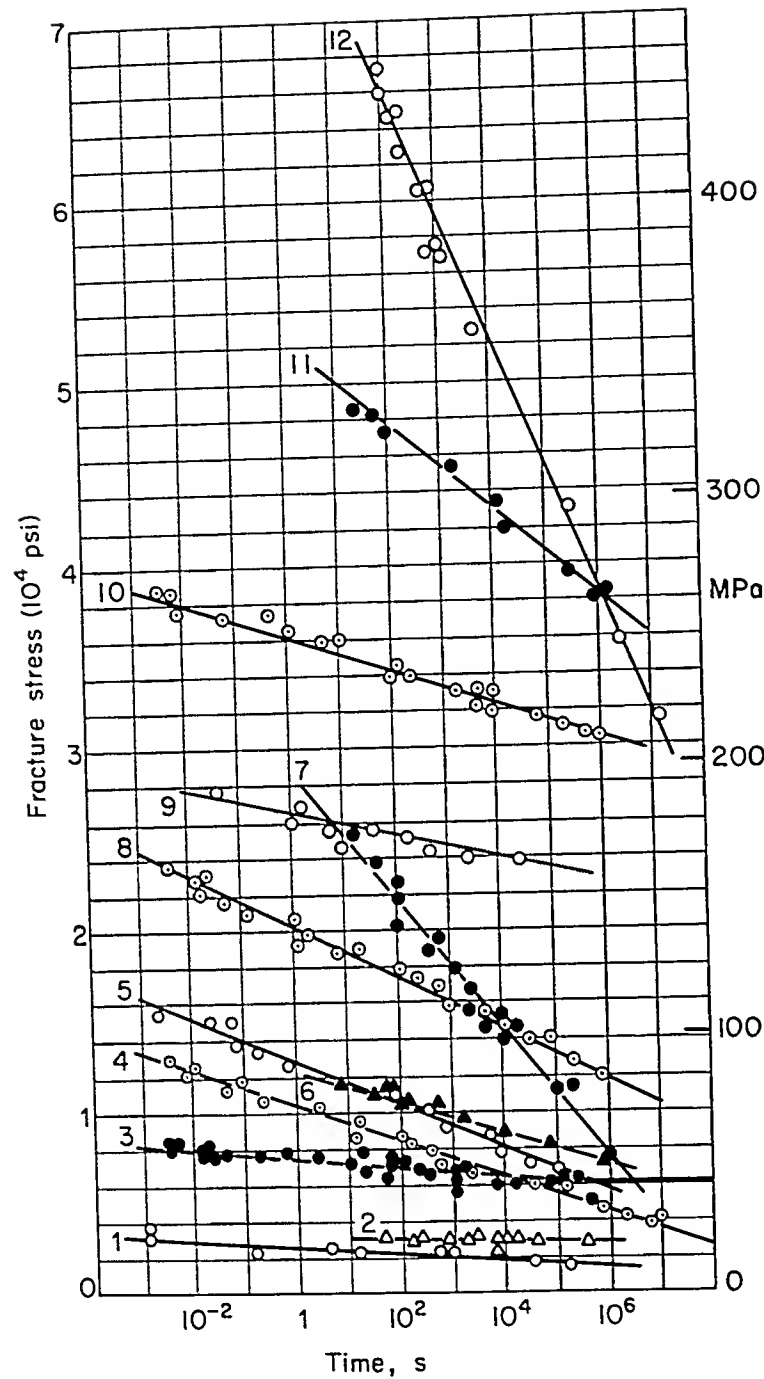


FIGURE 9-20

Time-dependent strength for polymeric and nonpolymeric materials [16]: 1, silver chloride; 2, polyvinyl chloride; 3, aluminum; 4, poly(methyl methacrylate); 5, zinc; 6, celluloid; 7, rubber; 8, nitrocelluloid; 9, platinum; 10, silver; 11, phosphoric bronze; 12, caprone (oriented).

they are now based on the cross section of the drawn fiber rather than on an originally spherulitic sample. Undrawn nylon 66 might typically have an ultimate tensile strength of 50 MPa at a breaking elongation of 200%. Based on the cross section of a drawn fiber, the tensile strength (tenacity) may be over 500 MPa. When a spherulitic material is stressed below T_g , the rearrangement to oriented crystallites becomes very difficult. Reding and Brown [18] found that in poly(chlorotrifluoroethylene) cracks tend to

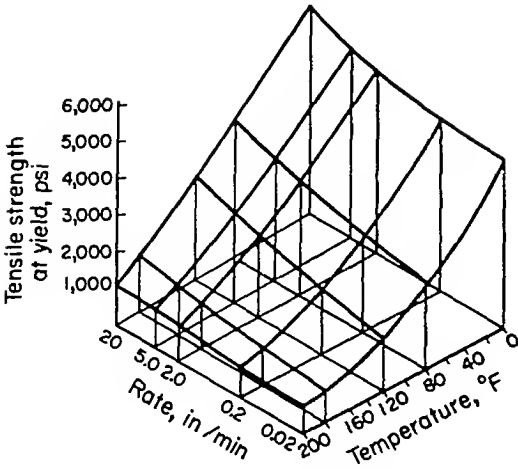


FIGURE 9-21
Effect of temperature and rate of extension on tensile stress at yield for an ethylene-butene copolymer [17].

propagate along the radii of spherulites and sometimes between two spherulites. For this reason, large, well-formed spherulites usually are avoided. Long-term creep tests leading to stress cracking in polyethylene that is above its T_g may involve spherulite growth also. These spherulites eventually reach the size of macroscopic flaws and can act as stress concentrators.

Since fibers consist primarily of oriented crystallites, perhaps it is unfair to classify them as heterophase. However, the generalizations regarding time-temperature superposition that work so well with amorphous polymers do not apply to fibers. Fibers do exhibit viscoelasticity qualitatively like the amorphous polymers. It comes as a surprise to some that J. C. Maxwell, who is best known for his work in electricity

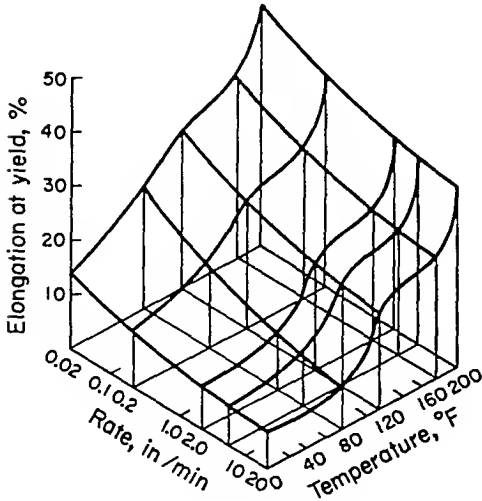


FIGURE 9-22
Effect of temperature and rate of extension on elongation at yield for the ethylene-butene copolymer of Fig. 9-21 [17].

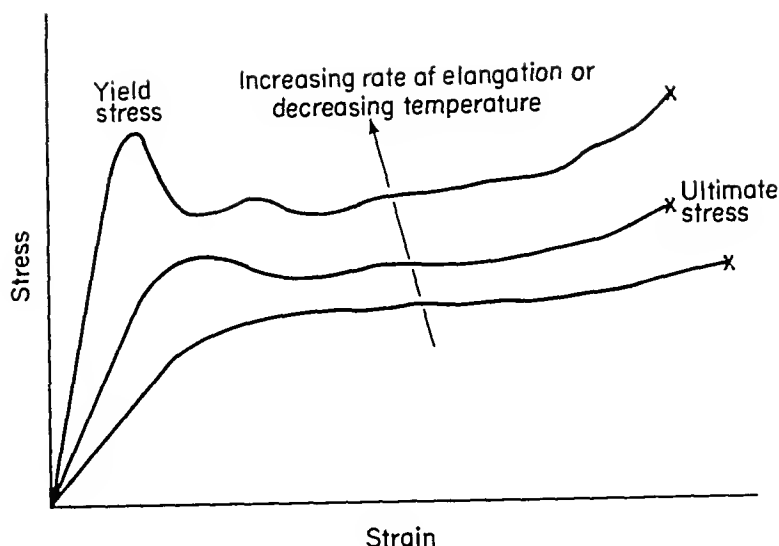


FIGURE 9-23

Typical stress-strain curves for polyethylene.

and magnetism, should have contributed to the mathematics of viscoelasticity. It was when he was using a fiber, a silk thread, as the restoring element in a charge-measuring device that he noticed that the material was not perfectly elastic and showed time effects. The model that bears his name was propounded to correlate the real behavior of a fiber.

The high melting temperature desirable in a crystalline fiber can be achieved by using a polar structure. Rayon, nylon, the polyesters, the acrylics, cotton, wool, and silk all contain ester, amide, or hydroxyl groups that can form strong hydrogen bonds. A corollary is that moisture and heat will almost always have a large effect on the physical properties of fibers that is magnified by the large exposed surface area. The terms used in the fiber industry for strength and diameter differ from those in other polymer industries. The *denier* of a fiber is the weight in grams of a unit 9000 m long. The *tenacity* is the ultimate stress expressed as grams (force) per denier. The relationship between density ρ (g/cm³), fiber diameter D (cm), strength σ_b (g/cm²), denier, and tenacity then is

$$\text{Denier} = 2.25 \times 10^5 (\rho D^2) \pi \quad (9-8)$$

$$\sigma_b = 9 \times 10^5 (\rho) \times (\text{tenacity}) \quad (9-9)$$

A fiber with a tenacity of 1 g/denier and a density of 1.11 g/cm³ has a respectable tensile strength of 10⁶ g/cm² (98 MPa or 14,200 psi). Nylon and silk show a uniform decrease in tenacity with increasing humidity, which is understandable in terms of a weaker crystal lattice with as much as 8% sorbed water competing for the hydrogen bonds (Fig. 9-24). Cotton, conversely, increases in tenacity as it sorbs up to 25% moisture, presumably because its cellular structure is able then to distort and allow more molecular chains to support stress along the major axis. Rayon, which is the same as cotton chemically but differs crystallographically, shows the more normal decrease with moisture at high humidities. The strengths indicated are for high-tenacity

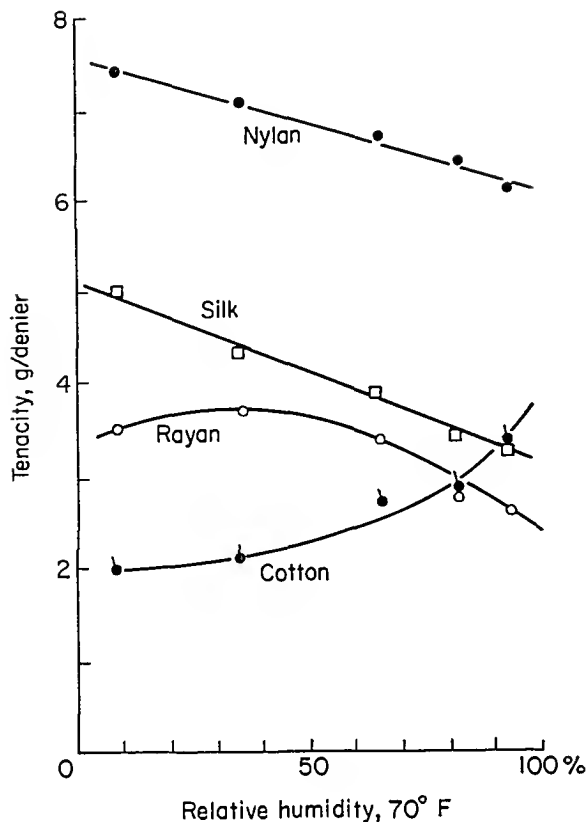


FIGURE 9-24

Strength vs. humidity for common fibers [19].

nylon and rayon. The overall balance of properties does not always make the strongest fiber the best for a particular application. The effect of temperature on rayon and nylon also reflects the relative stability of the hydrogen-bonded structure in each (Fig. 9-25).

Almost all applications of rubber make use of particulate fillers. Because automotive tires take about 70% of all the rubber consumed in the United States and because all tires are reinforced with carbon black, the economic importance of this one class of fillers becomes apparent. The term "reinforcement" implies an increase in the magnitude of some ultimate property. However, tensile strength is not the only property that may be reinforced. An improvement in tear strength, abrasion resistance, or fatigue may also justify the use of the term. The typical effect of carbon blacks on the ultimate tensile strength of natural rubber and a styrene-butadiene copolymer illustrates a basic difference in behavior of two classes of rubber (Figs. 9-26 and 9-27). Natural rubber crystallizes on stretching even though it may be well above its normal melting temperature (see Sec. 3-4). This is a reversible process in that the crystallites melt on release of the stress. The crystallites act as massive cross-links that spread the concentration of stress that would otherwise be located in a few bonds over a much wider area. Such a material is "self-reinforcing" in that it is stronger at a highly stressed point than elsewhere. At ordinary temperatures polychloroprene, some polyurethanes, polyisobutylene, and poly(propylene oxide) rubbers also are self-reinforcing, as evidenced by the fact that unfilled, cross-linked polymers of each can

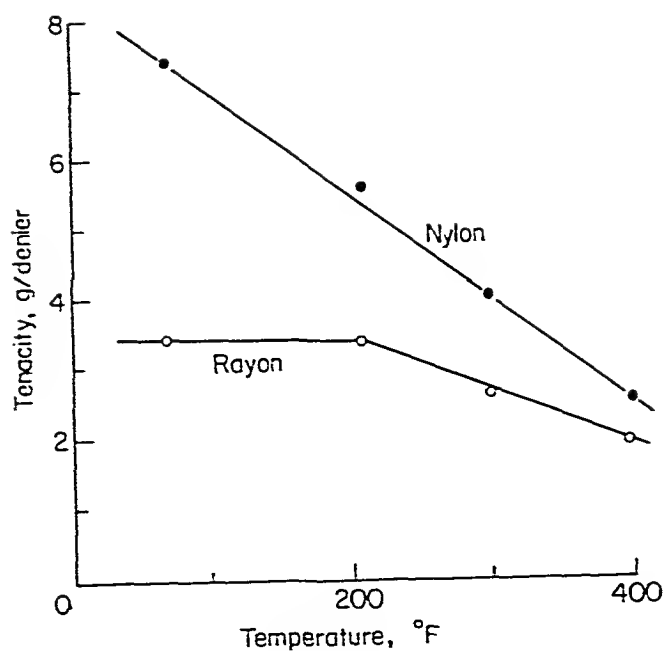


FIGURE 9-25
Strength vs. temperature for nylon 66 and rayon [19].

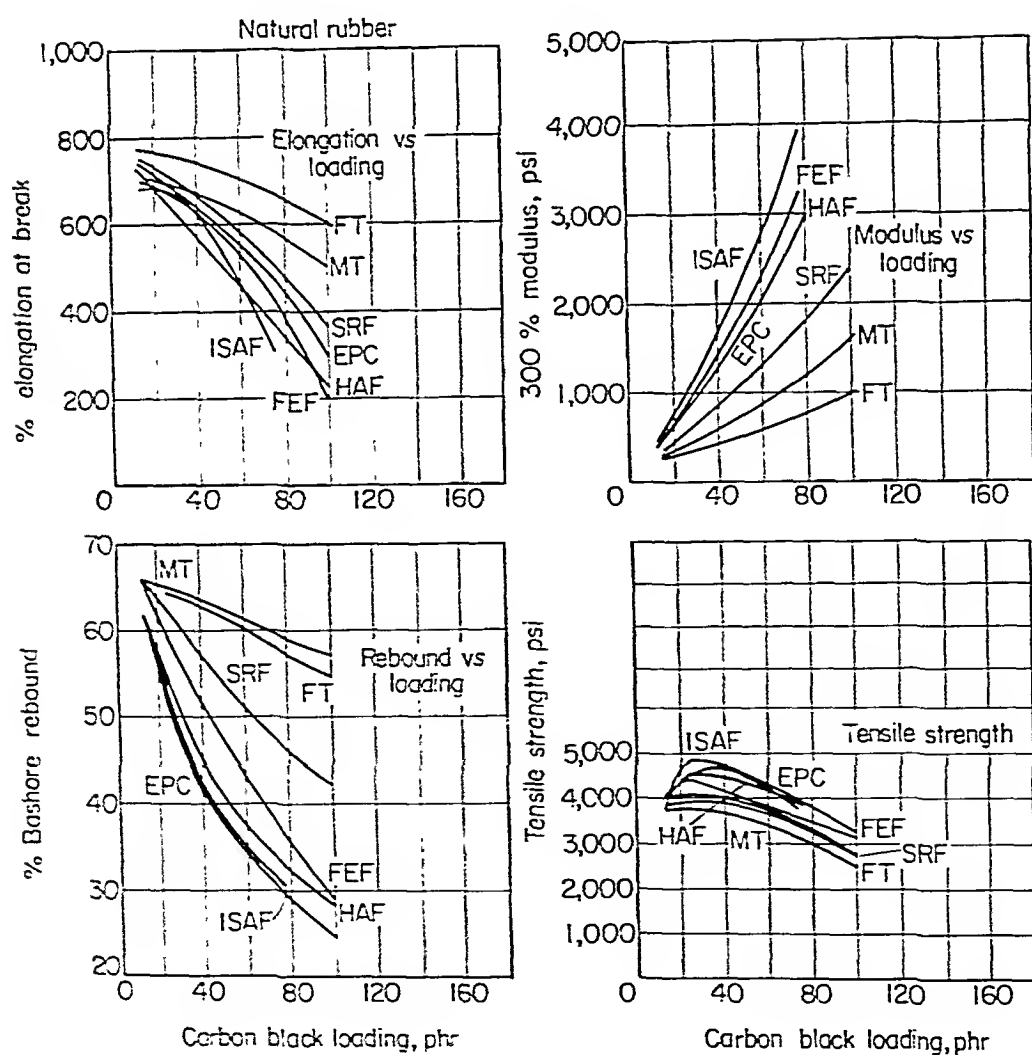


FIGURE 9-26
Properties of carbon-black-reinforced natural rubber vulcanizates [20]. Letters refer to specific black types; 1000 psi = 6.895 MPa.

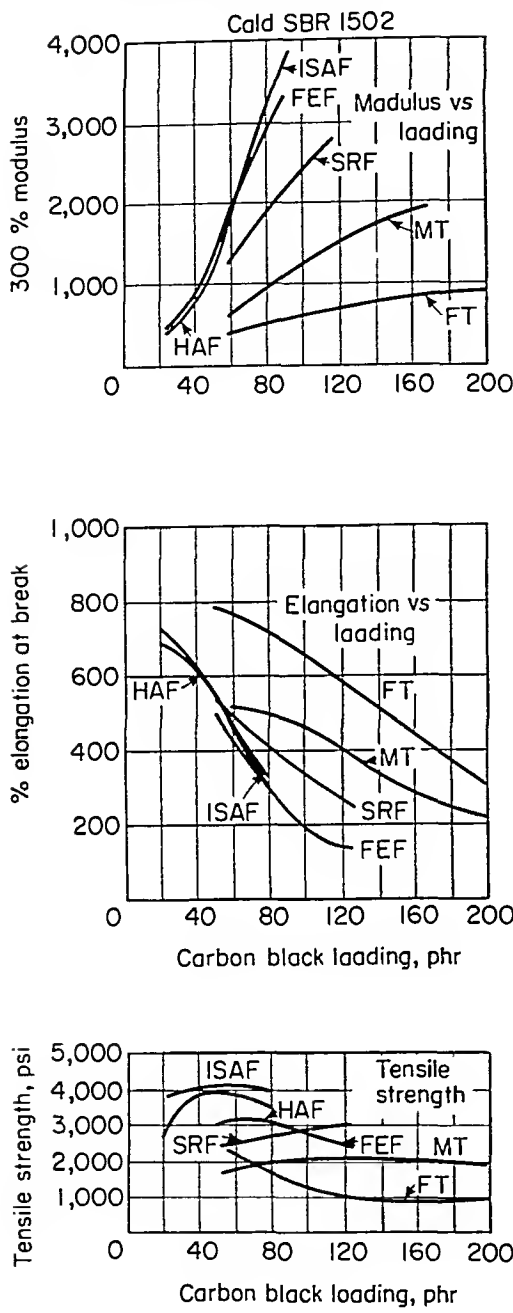


FIGURE 9-27
Properties of carbon-black-reinforced styrene-butadiene rubber (SBR 1502, cold rubber) vulcanizates [20]. Letters refer to specific black types; 1000 psi = 6.895 MPa.

be made with tensile strengths of over 20 MPa (2900 psi) with high elongations. Addition of fillers like carbon black increase tensile strength only slightly for this class of polymers, although tear strength may be improved greatly and abrasion resistance may be very much improved.

Rubbers that do not crystallize on stretching must be compounded with fillers to attain a tensile strength of more than a few MPa. The styrene-butadiene rubber

(Fig. 9-27) typifies this class, which includes poly(dimethyl siloxane), ethylene-propylene copolymers, and butadiene-acrylonitrile copolymers. It must be emphasized that we are speaking of typical behavior and relative changes in properties. Tensile strength and other properties are affected by cross-link density, temperature, and rate of testing, and other compounding ingredients (Sec. 10-2).

Ultimate properties are sample properties, and so the skill of the person making and testing the sample enters in also. Despite the many standardized procedures promulgated by the ASTM, among others, it is an incontrovertible fact that an experienced laboratory worker can always produce samples that outperform those put together by a neophyte using the same raw materials and equipment. The importance of the laboratory technician in providing reliable and reproducible characterizations should never be underestimated.

An unsophisticated rationalization of the fact that fillers (or crystallites) often increase tensile strength has been given by Bueche [21]. In a simple network (Fig. 9-28), the breaking of highly oriented strand *A* shifts the entire stress formerly borne by that strand to its few immediate neighbors. If they are near to the stress to rupture themselves already, they may break under the new added load and the flaw will propagate catastrophically. On the other hand, with a particle anchoring many strands, the load formerly borne by *A* can be shared among many strands rather than just the immediate neighbors (Fig. 9-28). The filler particle, in addition to acting as a cross-link, has the virtue of extremely high functionality, binding many chains to a rigid surface.

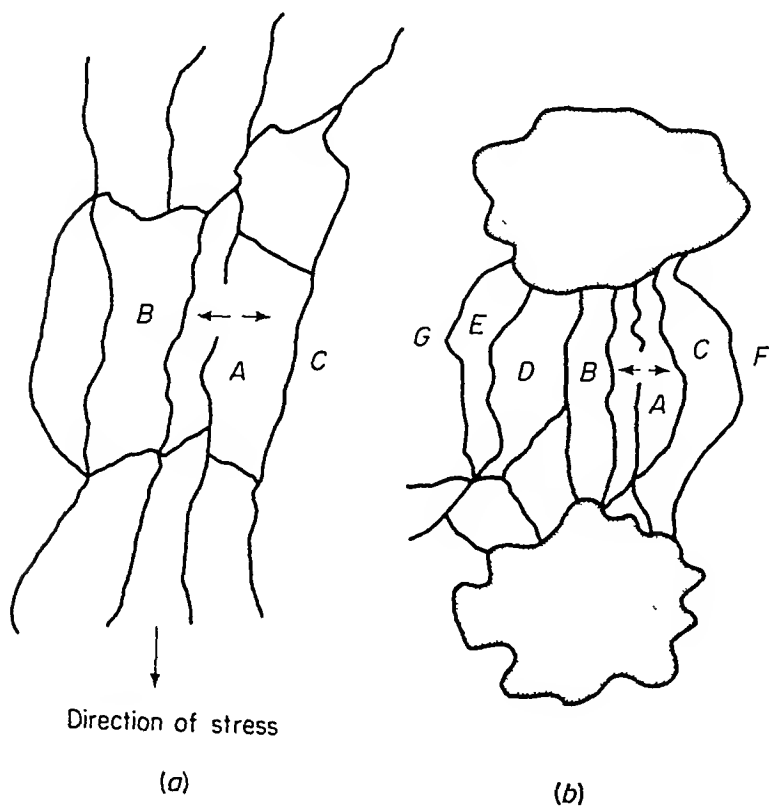


FIGURE 9-28

Stress-sharing mechanism for filler or crystallite reinforcement. (a) Polymer under stress without filler particles; (b) with filler particles or crystallites about 10 to 50 nm in diameter.

It is important that the filler be bonded to the polymer for this theory to apply. A test case is where polymer and filler are not similar chemically and thus have poor adhesion. Ethylene-propylene terpolymer and finely divided silica make such a system. Under the same conditions of mixing and cross-linking, a gum (unfilled) compound has a tensile strength of less than 1 MPa. A loading of 100 g of silica for 100 g of polymer raises this to 3.6 MPa. However, when the system is stressed, the polymer pulls away from the filler surface, forming vacuoles. Such vacuoles have been observed in carbon-black-filled systems under the electron microscope. An indirect effect that they have is to cause opacity, a whitening at the stressed point, due to the light scattered at the additional interfaces formed. The net volume of the system has to increase also as the result of vacuole formation. By placing a rubber band of the material in a dilatometer filled with water and stretching the band by means of a wire that issues through the capillary, one can measure the stress-strain behavior and the volume change as seen in the capillary section simultaneously (Fig. 9-29). When the polymer-silica band is extended, the volume does increase by a substantial amount (Fig. 9-30). However, if we incorporate a *coupling agent* that can react with the filler surface and with the polymer, we may be able to prevent the vacuole formation. Such a compound is a mercaptosilane:

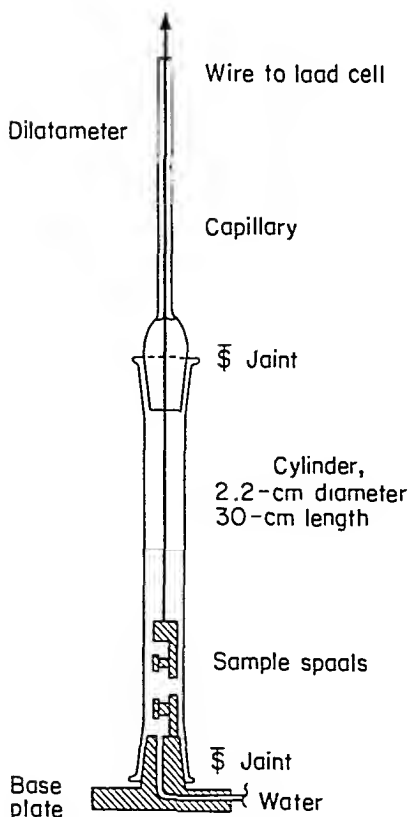
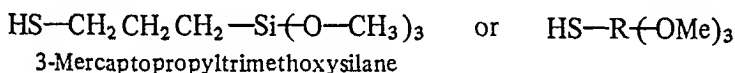


FIGURE 9-29

Dilatometer for measurement of volume during stretching of rubber [22].

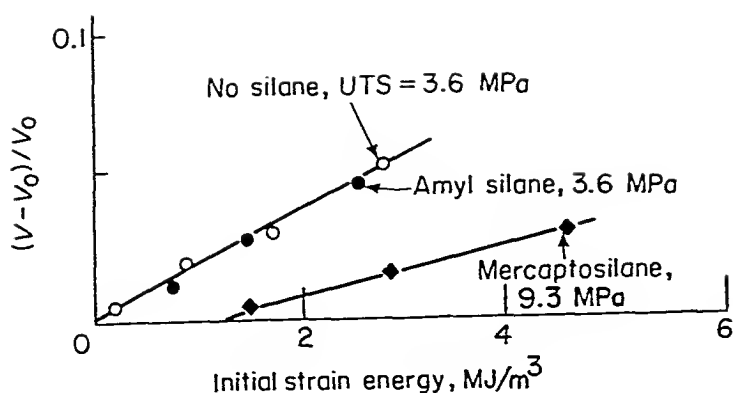
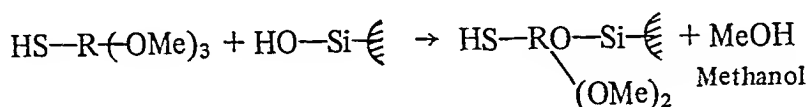


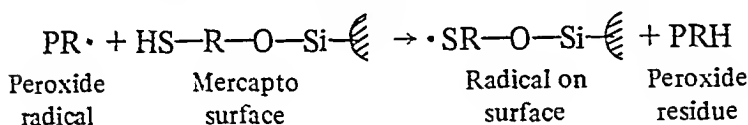
FIGURE 9-30

Change in volume on stretching for silica-filled, peroxide-cross-linked ethylene-propylene terpolymer [22].

We expect the filler, which is SiO_2 in the bulk but has a surface of $\text{Si}-\text{OH}$ groups, to react with the alkoxy portion of the coupling agent:



The mercapto portion can be expected to react during cross-linking:



The surface radical may add to a double bond of the polymer as in initiation of polymerization. If the mercapto functionality is absent, as in an amyl silane, no reaction with polymer should occur. It is obvious (Fig. 9-30) that the mercaptosilane has increased tensile strength and prevented the filler and polymer from parting at substantial energy inputs (area under the stress-strain curve). The amyl silane has no such effect.

In the carbon black reinforcement of rubber, the chemistry of the surface is important, as the previous work would indicate. The amount and functionality of oxygen, nitrogen, and hydrogen on the surface varies with the preparative method employed. Particle size itself is important, the generalization being that the finer the particle size the greater the reinforcement. Matters of ease of incorporation and fabrication as well as cost and other properties enter in to complicate the choice for any one application.

Particulate fillers are used also in adhesives and protective coatings. The function in the latter generally is pigmentation rather than reinforcement. Thermoset resins may be filled also, but the most common additive would be fibrous. The term *composites* has been applied to heterophase materials when the dimensions involved approach the macroscopic. Plywood and corrugated paper are two homely examples. Fibrous glass is used in several forms with polymers. As in the case of silica-reinforced

TABLE 9-1

Mechanical Properties of Glass-Reinforced Thermoplastics [23]

Material	Percent glass loading	Tensile strength, 73°F, psi × 1000 (D 638)*	Elongation, %, 73°F (D 638)	Flexural strength, 73°F, psi × 1000 (D 790)	Impact strength, notched Izod, 73°F ft·lb/in (D 256)	Heat distortion temp., °C at 264 psi (D 648)	Rockwell hardness (D785)	Specific gravity (D 792)
Nylon 6/10 raw								
Short fiber	30	8.5 17 to 19	85 to 300 3.0	22 to 26	1.2	—	R111	1.09
Long fiber	30	19.0	1.9	23	1.4 to 2.2 3.4	204 216	E35-45, R118 E70-75	1.30 1.30
Nylon 66 raw								
Short fiber	30	9.0	60 to 300	12.5	1.0 to 2.0	66 to 86	R108-R118	1.13 to 1.15
Long fiber	30	18.5 to 23 20	3.0 1.5	26.5 to 32 28	1.2 to 2.0 2.5	204 to 243 243	E50-55-R120 E60-70	1.37 1.37
Nylon 6 raw								
Short fiber	30	7.0	25 to 320	8	1.0 to 3.6	67 to 70	R103-R118	1.12 to 1.14
Long fiber	30	17 to 24 21.0	3 2.0	22.5 to 32 27	1.3 to 2.0 3.0	204 to 216 216	E45-50, M90 E55-60	1.38 1.37
Polycarbonate raw								
Short fiber	20	9.5	60 to 110	13.5	2.5	129 to 138	M70-R118	1.2
Long fiber	20	12 to 18.5 14 to 18.5	2.5 to 3 2.2 to 5	17 to 25 18.5	1.5 to 2.5 2.5 to 3.0	141 to 146 146	M92-R118 H80-90	1.35 1.35
Polypropylene raw								
Short fiber	20	4.3	200 to 700	6		57 to 63	R85-110	0.90 to 0.91
Long fiber	20	6.0 8	3.0 2.2	7.5 10	1.0 3.5	110 139	M40 M50	1.05 1.05
Polyacetal raw								
Short fiber	20	10.0	15	14	1.4	124	M94-R120	1.425
Long fiber	20	10 to 13.5 10.5	2 to 3 2.3	14 to 15 15	0.8 to 1.4 2.2	157 to 163 163	M70-75-95 M75-80	1.55 1.55
Polyethylene raw							(Shore)	
Short fiber	20	1.2	50 to 600	4.8	0.5 to 16	32 to 41	D50-60	0.92 to 0.94
Long fiber	20	6 6.5	3.0 3.0	7 8	1.1 2.1	107 127	R60 R60	1.10 1.10
Polysulfone raw								
Short fiber	30	10.2	50 to 100		1.3	174	M69-R120	1.24
Long fiber	30	16 18.5	2 2.0	21 24	1.8 2.5	182 167	— E45-55	1.41 1.37

* ASTM test method. Note: Most favorable figures for short-fiber performance are based upon results with nominal $\frac{1}{8}$ -in fibers. Not included in the table are glass-reinforced styrene, SAN, ABS, polyurethane, and PPO, for which comparable data between short and long fibers are not available. 10^3 psi $\approx$ 6.895 MPa.

rubber discussed above, coupling agents are useful to promote adhesion between the glass, which is about 50% SiO_2 and 50% oxides of aluminum, calcium, and other cations. The surface contains hydroxyl groups that can react with alkoxy silanes. The organofunctional alkyl group on the silane is tailored to react with the particular polymer.

Chopped strands 1 to 10 mm in length can be incorporated in thermoset or thermoplastic materials about as easily as the particulate fillers. Each strand may be made up of 204 individual filaments whose diameter is 5 to 20 μm . Since the modulus of the "E-glass" most often used is 10.5×10^5 psi (724 GPa) and the tensile strength upwards of 250,000 psi (2 GPa), it is not surprising that the stiffness and strength of most plastics can be increased by compounding with glass. In looking at the effect of glass on tensile and flexural strength of the nylons (Table 9-1), the sacrifice in elongation should not be ignored. The total energy that can be absorbed by the system before failing is much smaller for nylon 66 with glass, for example, than without, as indicated by the product of stress and elongation at break. Even at very short test times, the impact strength is not changed. On the other hand, the designer of a nylon gear or wheel has no need for high elongation, so that the dimensional stability (higher modulus and higher heat distortion temperature) and added strength are obtained at the loss of a property he did not particularly cherish from the beginning.

Chopped strands of glass several inches long can be loosely bound as a mat which is porous and in which the strands are randomly oriented in two dimensions. This form is suitable for impregnation by a liquid prepolymer. After polymerization or cross-linking (curing) under pressure, the composite will comprise a network-polymer matrix in which are embedded the individual strands. A woven glass cloth might be used in place of the mat or in combination with it. In this case there will be a variation in strength with the angle between the axis of the fibers and the direction of stress (Fig. 9-31). The filament-wound structure represents the ultimate in directional strength (Fig. 9-32). With careful fabrication and with the aid of coupling agents, the

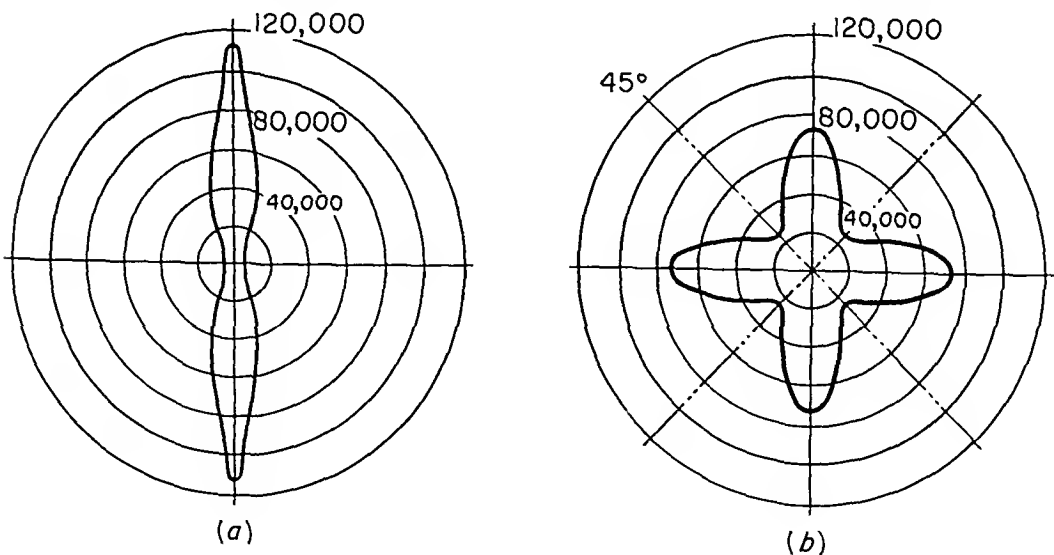


FIGURE 9-31

Tensile strength as a function of direction for fiber-reinforced plastics [24]. (a) Unidirectional fibers; (b) cross-ply fibers; 1000 psi = 6.895 MPa.

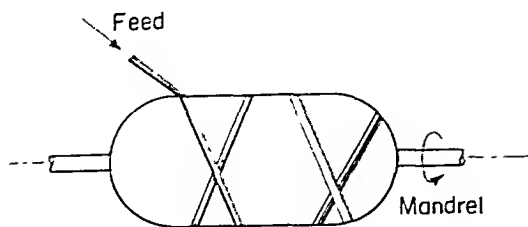


FIGURE 9-32

A cylindrical pressure vessel being fabricated by winding glass filaments over a mandrel.

tensile strength of the glass is approached. In one glass-reinforced polyester system, the ultimate flexural strength varied with treatment. The resin itself had a strength of only 115 MPa (16.7×10^3 psi) compared to 924 MPa (134×10^3 psi) for an untreated glass-resin filament-wound ring. With proper sizing and with application of a vinyl silane coupling agent, the strength rose to 1.17 GPa (170×10^3 psi). In this last condition, the system was 87% glass by weight (75% by volume). In some applications where weight is important, the ratio of the strength to the density of a material becomes a dominant factor. The ratio of strength divided by density, the *specific strength*, is often expressed in inches when the engineering system of units is used. For the composite just described, a strength of 170×10^3 lb_f/in² divided by a density of 0.077 lb/in³ yields a specific strength of 2.2×10^6 in. The “cancellation” of pounds mass by pounds force is a delightful peculiarity of the older system of units. In SI units, the specific strength for the same material is 550 kJ/kg. A high-strength steel alloy would have a specific strength about one-third that of the composite [25].

Another kind of composite is the polymer “alloy.” Two polymers of marginal compatibility and widely differing moduli will act somewhat like the glass and polymer, having a rigid, load-bearing element and at the same time a softer, energy-absorbing element. Styrene-butadiene copolymer ($T_g = -50^\circ\text{C}$) is combined with polystyrene ($T_g = +100^\circ\text{C}$) to give a “rubber-reinforced” plastic. In long time-scale tests such as ordinary tensile testing, the rigidity and strength of pure polystyrene are approached. However, in a rapid test, such as the Izod impact test, the rubbery portion will deform, absorbing much more energy than the brittle polystyrene would have. The toughness of alloys together with their dimensional stability makes them quite versatile. Some other examples are butadiene-acrylonitrile copolymer in poly(vinyl chloride) and acrylonitrile-butadiene-styrene (ABS) terpolymer with polycarbonates. Applications include refrigerator door liners, radio and TV cabinets, pipe and fittings, and women’s shoe heels.

PROBLEMS

- 9-1. Three different rubber compositions give the following strengths in a standard tensile test:

Sample	Strength for compositions, psi		
	A	B	C
1	3300	2310	1660
2	3250	2310	1600
3	3125	2200	1600
4	3000	2150	1510
5	2850	1990	1325

Are any samples atypical? If a fourth composition were run and gave a value of 2000 psi for a single sample, how confident would you be that this was the average strength?

- 9-2. For a very large population of samples ($N = 10^4$), what fraction of the population will have a tensile strength greater than $\bar{\sigma}_b + s$? What fraction will have a tensile strength greater than $\bar{\sigma}_b - s$ and $\bar{\sigma}_b - 2s$?
- 9-3. For the average performance indicated by the solid lines in Figs. 9-8 and 9-10, plot breaking stress vs. time to break in the manner suggested by Fig. 9-20. How does the slope compare with the slopes for other polymers? How important is the elongation at break in this kind of plot?
- 9-4. Why does the addition of glass fibers increase the heat-distortion temperature of crystalline polymers, such as polyethylene and polypropylene, but not of glassy ones, such as polycarbonate and polysulfone (Table 9-1)?
- 9-5. What is the "true" stress at break based on actual cross section for SBR rubber loaded with FT black (Fig. 9-27) as a function of black loading? What is the corresponding strength in grams per denier assuming a density that is the weighted average of that for rubber (0.94 g/cm^3) and that for carbon black (1.8 g/cm^3)?
- 9-6. An amorphous polymer can be approximated by a Maxwell element in which a spring flies apart when it reaches some maximum elongation ϵ_{sb} . Show how this model leads to a typical failure envelope. Why is this model inadequate for a cross-linked SBR rubber?

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10

SOME GENERAL PROPERTIES OF POLYMER SYSTEMS

10-1 DESIGN CRITERIA

The final judgment on the suitability for a polymer for a given application usually involves a complex combination of properties. Some of these properties are inherent in the physical state of the polymer. A glassy material will not stretch, nor will an un-cross-linked, amorphous polymer support a stress indefinitely when it is above its T_g . Some properties are inherent in the chemical structure of the polymer. Hydrolysis, thermal dissociation, and toxicity may be fixed by the reactivity of certain groups within the polymer structure.

In any application, cost is an important factor. The price of the polymer in the form of a powder, latex, solution, or bale is just part of the economic picture. The cost of other ingredients, equipment for fabrication, labor, power, and all the indirect costs, may well overshadow the polymer's share. A first-line tire containing the best rubber sells for 10 to 20 times the cost of the raw rubber it contains. Even in a much less complicated structure, such as plasticized poly(vinyl chloride) laboratory tubing, the raw material cost may be less than one-tenth of the selling price.

Some properties that might be considered for a single application are [1]:

Appearance	Rigidity
Hardness	Creep and cold flow
Density	Fatigue
Mechanical properties:	Dimensional stability
Tensile strength	Durability
Compressive strength	Thermal properties:
Flexural strength	Coefficient of expansion
Shear strength	Thermal conductivity
Impact resistance and	Specific heat
toughness	Heat-distortion temperature

Thermal properties (<i>Continued</i>):	Dielectric constant
Heat resistance	Power factor
Flammability	Arc resistance
Electrical properties:	Chemical resistance to:
Resistivity	Acids, bases, solvents, oils,
Dielectric strength	and fats

10-2 COMPOUNDING

The polymer characteristics we have discussed so far are useful guideposts in predicting the behavior of polymers in real applications. However, a lacquer is not an “infinitely dilute” solution, nor is a tire composed of “ideal” rubber. In many useful systems the polymer is one of several constituents, and perhaps not the most important one.

The largest volume synthetic rubber today, styrene-butadiene rubber (SBR), is a prime example of the complexities of polymer *compounding* for real life. By compounding we mean the mixing of polymer with other ingredients. In SBR these can be:

1. *Reinforcing fillers*. These improve tensile strength or tear strength. Carbon black and silica are typical.
2. *Inert fillers and pigments*. These may not change final properties in a desirable direction, but they may make the polymer easier to mold or extrude and also lower in cost. Clay, talc, and calcium carbonate are used.
3. *Plasticizers and lubricants*. Petroleum-based oils, fatty acids, and esters are most often used.
4. *Antioxidants*. These generally act as free-radical “sinks” and thus stop the chain reactions in oxidation.
5. *Curatives*. These are essential to form the network of cross-links that guarantee elasticity rather than flow. Sulfur for unsaturated and peroxides for saturated polymers are used with auxiliaries to control reaction rate.

One may ask why all this is necessary, since SBR (cross-linked) is almost an ideal rubber as defined earlier. The trouble with this “ideal” material is that it does not extrude smoothly, it degrades rapidly on exposure to warm air, and it has a tensile strength of about 500 psi (3.5 MPa). Proper compounding changes SBR to a smooth-processing, heat-stable rubber with a tensile strength of over 3000 psi (20 MPa)! However, theoretical equations no longer describe its mechanical behavior. The *compounder* then must be part scientist, part artist, and part statistician if he is to develop optimum properties in a material. It is virtually impossible to optimize all properties at once, so compounders have developed specialized “recipes” for girdles, tires, fan belts, tarpaulins, electrical insulation, etc. Over 9000 such recipes were *published* between 1948 and 1957 alone!

Figure 10-1 illustrates the means by which compounders have attempted to shorten the work of *formulation*. A grid of data points is determined experimentally and a “contour map” is prepared. A mathematical counterpart can be obtained with the help of a computer [2]. While such techniques are helpful, the experience of the compounder and his willingness to innovate usually determine his effectiveness.

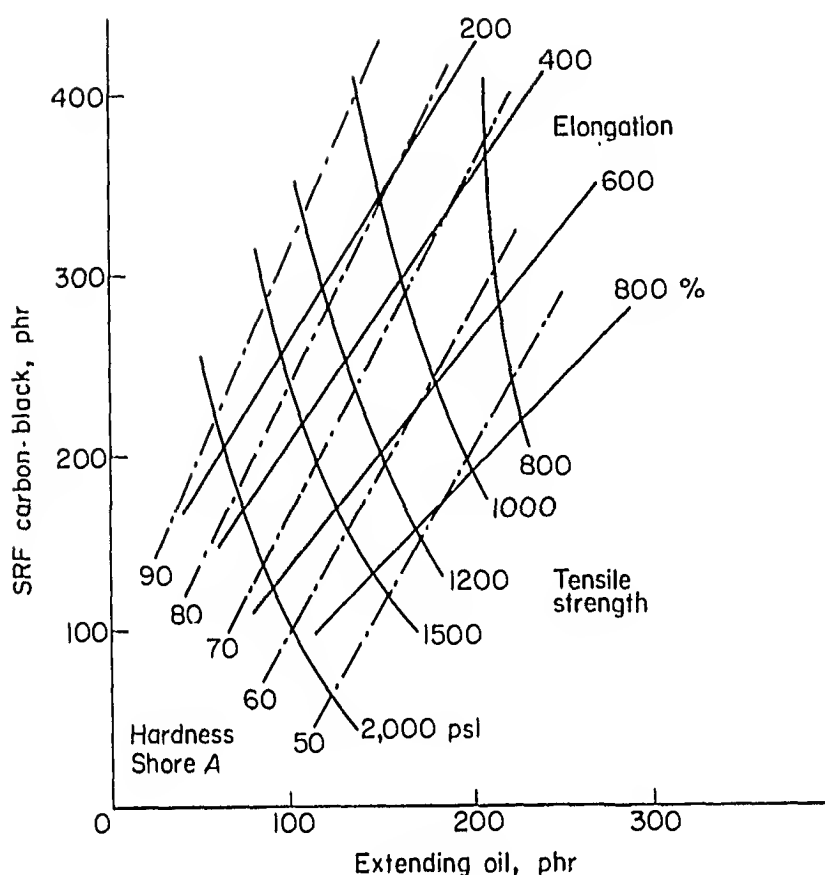


FIGURE 10-1

Typical contour plot to abbreviate compounding data [3]. Note that a compound with 200 *parts* each of oil and filler *per hundred* parts of rubber by weight (phr) still has a strength of about 1000 psi (7 MPa), quite acceptable for many mechanical applications. The compound, based on a high-molecular-weight ethylene-propylene terpolymer, also contains 5 parts zinc oxide, 1 part stearic acid, 1.5 parts sulfur, 1.5 parts tetramethyl thiuram disulfide, and 0.5 parts of benzthiazyl disulfide. Cross-linking takes place at 160°C for 20 min.

Mixing machines for polymers vary from ball-and-pebble mills that disperse pigments in low-viscosity paints over periods of hours and days to heavy “internal mixers” that may use 1500 hp (about 1100 kW) to disperse 100 kg of carbon black in 200 kg of rubber in about 10 min.

One might divide polymer applications into those that involve extensive compounding and those that do not. Of course, there are many exceptions.

Generally compounded

Rubber
Thermosets
Adhesives
Protective and decorative coatings

Generally not compounded

Fibers
Thermoplasts (PVC is a wild exception)

In the case of fibers, the art of compounding is of less importance than the art of *aftertreatment*. Dyeing, texturing, and fabrication of textiles are complex processes that can obscure the ideal properties of polymers in the final product.

10-3 HARDNESS

The most common measure of hardness is the distance into the material that a steel ball will penetrate under a specified load. A spring-loaded, ball-tipped indenter may be used so that the stress is not a linear function of penetration. Since the measurement is basically a compressive modulus, one expects stiff materials to be hard and flexible materials to be soft. In choosing a material for a gasket, hardness often is the only specification listed.

Surface hardness is also measured by scratch and abrasion resistance. As a rule, polymer systems cannot approach the surface hardness of silica glass, which is itself a highly cross-linked structure. Some highly cross-linked laminates do have scratch resistance nearly like that of glass.

10-4 DENSITY

Polymers and other ingredients of polymer systems are sold on a weight basis. However, in most applications they compete on a volume or strength basis. On a strength-volume basis a reinforced plastic sheet may prove much more economical for an aircraft seatshell than a metal sheet that sells for one one-hundredth as much on a pound basis. Several factors affect density including pressure, temperature, and crystallinity.

It has been pointed out that specific volume increases with temperature for polymers, especially where melting occurs. Since crystallinity involves a closer packing of molecules than glassiness, density can be used to measure crystallinity. The specific gravity of polyethylene, for example, varies from 0.86 (extrapolated from the melt) when amorphous to 0.98 when highly crystalline at 25°C [4]. The effect of pressure is important in molding processes where the high molding pressures alter the dimensions of a piece from what they will be at one atmosphere. High pressures that increase density also increase viscosity, because less "free volume" is available for segmental motion (see Sec. 7-5). In a molding operation just above the normal melting temperature, a high pressure may induce crystallization, which stops flow altogether. In Fig. 10-2 the compressibility of an amorphous polymer, polystyrene, is shown together with the compressibility of branched and linear polyethylene. Compressibility is expressed here as the change in volume $\Delta V/V_R$, where V_R is a reference volume at 1 atm and 75°F (23.9°C). The sudden change in volume with pressure for polyethylene is due to crystallization. The change is greater with linear than with branched polymer, because the degree of crystallinity induced is greater. Also illustrated in Fig. 10-2 is the fact that compression of a polymer is time-dependent too. When polystyrene is injection-molded at a pressure of 10,000 psi (69 MPa), there can be a significant difference in final dimensions of the piece depending on the length of time the melt is under pressure before cooling below T_g .

The atomic makeup of polymers affects density in much the same way it does low-molecular-weight compounds (Table 10-1). It should be remembered that a typical linear polymer is 15 to 30% more dense than the corresponding monomer.

The density of final compounded products usually is the weighted average of the ingredients (provided none are volatilized during fabrication). Some examples are given in Table 10-2.

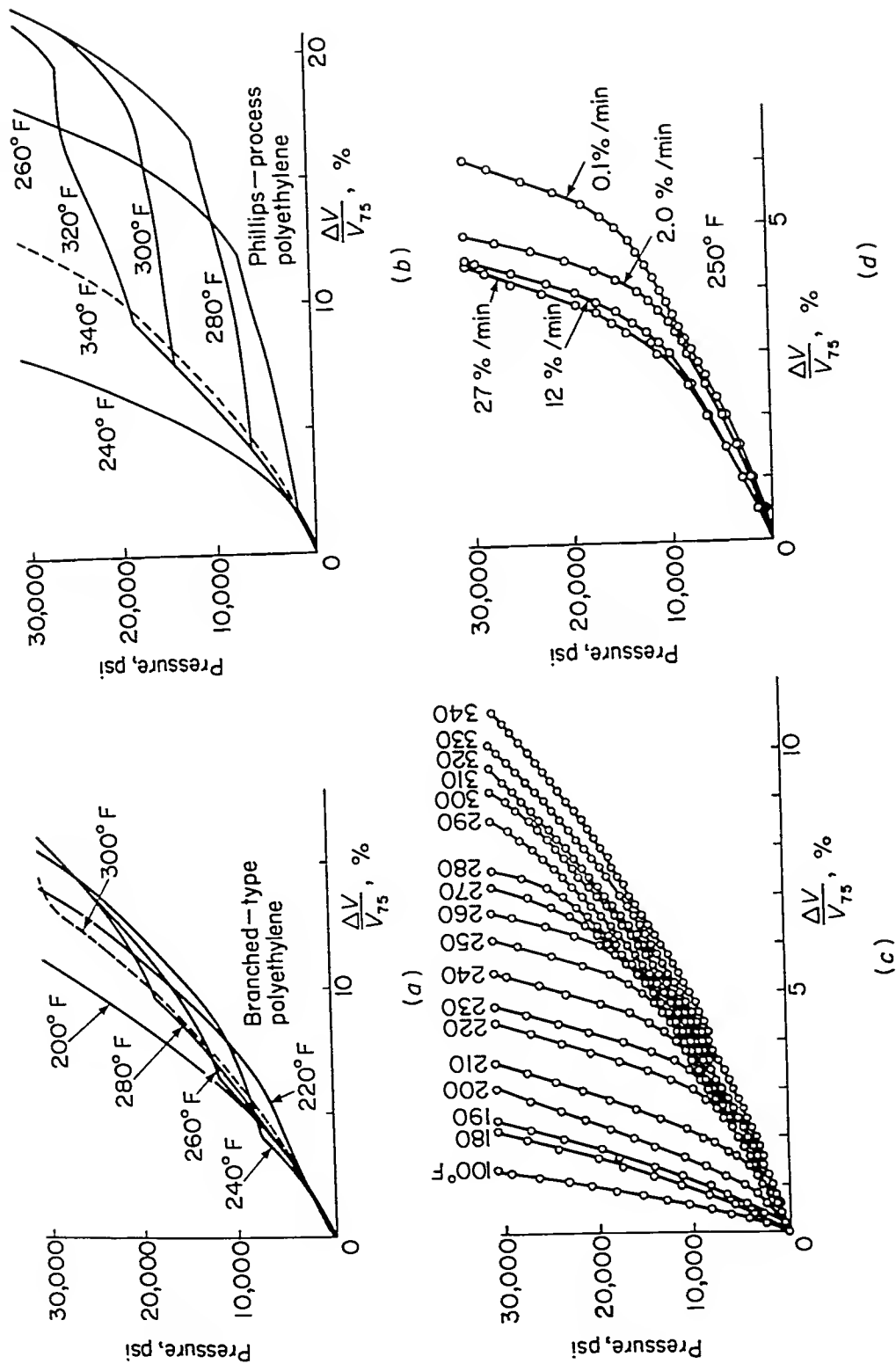


FIGURE 10-2
The abrupt changes in slope for polyethylene as it is compressed indicate crystallization. Linear polyethylene crystallizes to a greater degree than the branched polymer. The compressibility also is rate-dependent, as seen in (d). $\Delta V/V_{75}$, %, is the change in volume from 1 atm to the pressure indicated times 100/(volume at 75°F, 1 atm) [5]; 1000 psi = 6.895 MPa.

TABLE 10-1
Specific Gravity of Polymers

Chemical composition of polymer	Typical specific gravity of pure polymer near room temperature
Aliphatic hydrocarbons (polyethylene, polyisoprene)	0.8-1.0
Aromatic hydrocarbons and silicones (polystyrene)	1.0-1.1
Oxygen and nitrogen-containing polymers (cellulosics, polyesters, polyamides)	1.1-1.4
Chlorinated polymers	1.2-1.8
Fluorinated polymers	1.8-2.2

10-5 THERMAL PROPERTIES

Many polymers have a coefficient of linear thermal expansion α_e in the range of 2 to 20×10^{-5} cm/cm $\cdot^\circ$ C, compared to steel at about 1×10^{-5} . This complicates the design of molds for precision parts and the design of metal inserts in polymer parts. Of course, α_e varies with the state of the polymer, as indicated earlier in comments on the variations of specific volume at T_g and T_m (Sec. 3-4). Replacement of polymer by less expansile fillers lowers the overall expansion.

Thermal conductivity k_c of polymers is uniformly low. Values of $k_c = 0.05$ to $0.20 \text{ Btu/ft}\cdot\text{h}\cdot^\circ\text{F}$ are common.

$$\frac{242 \text{ Btu}}{\text{ft} \cdot \text{h} \cdot ^\circ\text{F}} = \frac{1 \text{ cal}}{\text{cm} \cdot \text{s} \cdot ^\circ\text{C}} = \frac{419 \text{ watt}}{\text{m} \cdot ^\circ\text{C}}.$$

Conductivity is not easily increased. A high concentration of a metal in powder or fiber form can raise it perhaps tenfold. In Table 10-3 the thermal conductivity of the base resins can be increased by aluminum or copper metal. These also increase electrical conductivity. If low electrical conductivity (for example, 10^{-16} S) is desired, the mixture of aluminas can give a high thermal conductivity. Foaming with air or some other gas is used to decrease thermal conductivity. A foamed polystyrene with a

TABLE 10-2
Specific Gravity of Filled Polymers

Parts by weight	Polymer	Specific gravity	Parts by weight	Filler	Specific gravity	Final specific gravity
100	Natural rubber	0.93	50	Carbon black	1.8	1.1
100	Natural rubber	0.93	100	Calcined clay	2.6	1.4
100	Epoxy resin	1.2	200	Glass fibers	2.5	1.8
100	Phenolic resin	1.3	100	Wood flour	0.9	1.1
100	Polyurethane	1.2	900	Nitrogen		0.12
			(pts by vol)			

TABLE 10-3
Thermal Conductivity of Various Filled Epoxy Resins [6]

Filler	Volume percent of filler in compound	Thermal conductivity cal/cm·s × 10 ⁴		
		Filler	Base resin	Filled compound
Aluminum, 30 mesh	63	4970	4.7	60.4
Sand, coarse grain	64	28	4.7	23.6
Mica, 325 mesh	24	16	4.7	12.2
Alumina, tabular	53	723	4.7	24.5
Alumina, 325 mesh	53	723	5.4	34.0
Copper powder	60	9180	5.4	39.0
Silica, 325 mesh	39	28	5.4	18.3
Mixture of:				
Alumina, tabular (20 to 30 mesh)	45	723	4.7	58.8
Alumina, 325 mesh	20			

density of 2.5 lb/ft³ and a $k_c = 0.02$ Btu/ft·h·°F is useful as insulation for a variety of applications from picnic baskets to boxcars. The variation of k_c with density and average temperature is shown in Fig. 12-54.

A *specific heat* of 0.4 ± 0.1 cal/g·°C is typical for unfilled polymers. Composites generally have the average specific heat of the components. This is another property that varies with the physical state of the polymer in relation to T_g and T_m .

The yielding of a polymer under load or under its own weight usually occurs at a *deflection temperature* that is in the vicinity of T_g or T_m . The older term *heat distortion temperature* is still used in many places.

Flammability is a function of physical form and chemical composition. An air-foamed material or a thin film presents extensive surface for burning compared to a heavy solid section. Chemical composition has the same effect that it has with lower-molecular-weight compounds. In general we can rank pure polymers as follows:

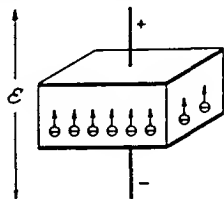
Most flammable: Nitrated polymers
 Oxygen-containing polymers
 Hydrocarbon polymers
 Polyamides
 Least flammable: Halogenated polymers

Certain plasticizers (phosphate ester and halogenated waxes) and fillers (antimony trioxide combined with chlorinated hydrocarbons) can contribute flame resistance. On the other hand, nitroglycerine is an ideal plasticizer for nitrocellulose when the objective is to maintain the flammability of a rocket propellant [7].

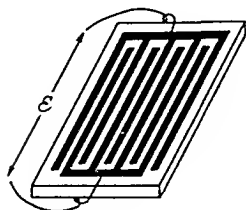
10-6 ELECTRICAL PROPERTIES

Resistance is a familiar electrical property. The *volume resistivity* ρ_r is the resistance in ohms of a material 1 cm thick, t , and 1 cm² in area, A (Table 10-4). The resistance R of any other configuration is given by

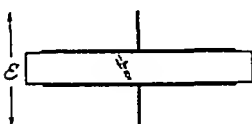
TABLE 10-4
Electrical Properties [8]



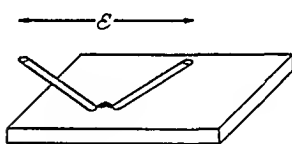
Volume resistivity is the ohmic resistance of the bulk dielectric material measured as though the material were a conductor. The resistance is expressed as the resistance of a cube 1 cm on a side measured between faces. This value is measured according to ASTM D 257. It is dependent on temperature, frequency, and voltage and will vary with the conditioning of the material.



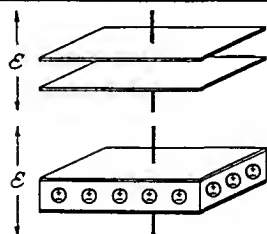
Surface resistivity is defined as the resistance between two electrodes on the surface of an insulating material. It obviously can be measured only on materials having high intrinsic volume resistivity as a reduction of resistance. The units are ohms per square centimeter, and the test method is ASTM D 257. The value is dependent on temperature, frequency, and voltage, but is most affected by the humidity- and moisture-conditioning cycles to which it has been subjected, all of which must be given with the value.



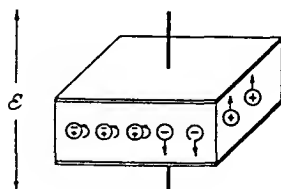
Dielectric strength is defined as the potential per unit of thickness that will cause catastrophic failure of a dielectric material. This value is measured according to ASTM D 149. The value is dependent on the method of application of potential, the nature of the potential, dc or frequency of ac, and the temperature, and it varies with the conditioning of the specimen, all of which must be specified with the value.



Arc resistance is the time in seconds that an arc may play across the surface of a material without rendering it conductive. The property is measured according to ASTM D 495 with the low-current, high-voltage arc. The failure may occur by carbonization, heating, and other means, and it is dependent on temperature, frequency, and conditioning, which, as well as the type of failure, must be specified.



Dielectric constant is defined as the ratio of the capacity of a condenser made with a particular dielectric to the capacity of the same condenser with air as the dielectric. The test method for plastics is ASTM D 150. The value is frequency- and temperature-dependent and varies with conditioning, all of which must be specified with the value.



Dissipation factor is the ratio of the real power (in-phase power) to the reactive power (power 90° out of phase). It is related to the power factor, which is the ratio of the real power to the voltage-ampere product by the relation

$$\text{Dissipation factor} = \frac{\text{power factor}}{\sqrt{1 - \text{power factor}^2}}$$

Loss factor is the product of the dielectric constant and the power factor and is a measure of signal absorption. The dissipation factor is a measure of the conversion of the reactive power to real power, showing as heat. The mode of heating can be by electron or ion flow and by dipole rotation. It is variable with frequency, temperature, conditioning, and potential. The test method is ASTM D 150, and the conditions of the test and frequency must be specified.

$$R = \frac{\rho_r t}{A} \quad (10-1)$$

In the case of an insulated cable with inside radius R_1 and outside radius R_2 and length L ,

$$R = \frac{\rho_r}{2\pi L} \ln \frac{R_2}{R_1} \quad (10-2)$$

High values of resistivity are common for organic polymers, 10^{12} to 10^{18} ohm·cm being typical. The actual value of resistivity depends on frequency and voltage. It decreases with increasing temperature. In any polymer system, fillers or absorbed water may provide conductive paths.

Electrical resistance can be lowered markedly by the addition of conductive fillers. A novel application involves the use of a conductive, elastic silicone rubber as a metal-free ignition wire in automobiles. Certain carbon blacks impart conductivity:

Carbon black (Vulcan XC-72, Cabot Corp), parts by wt/100 parts of rubber	Volume resistivity, ohm·cm
0	10^{14}
15	10^4
60	10

With silver-coated metal powder as a filler, resistivities of 10^{-4} ohm·cm are possible. A low resistivity often is desirable to prevent the accumulation of static charges, which can be merely annoying in clothing or carpeting but very dangerous in the presence of a combustible gas as in a hospital operating room. Plastic tile floors for such rooms are often compounded with conductive fillers.

Surface resistivity (Table 10-4) is especially important when the fabricated article may be subjected to a high humidity, which can alter the surface physically or chemically to give a lower resistance than the bulk of the material.

Dielectric strength (Table 10-4) is analogous to tensile strength. The voltage on a thin slab of material held between two electrodes is increased until catastrophic failure occurs, usually burning a hole completely through the slab. The shape of the electrodes, the rate of increase of voltage, and the thickness of the slab all affect the dielectric strength. Values of several hundred volts for a thickness of 25 μm are not uncommon.

Arc resistance (Table 10-4) of a polymer that decomposes to volatile products in the presence of an arc usually is better than for a polymer that is reduced by the arc to conductive carbon. For example, poly(methyl methacrylate) is "nontracking" because it depolymerizes to monomer (see Sec. 11-3).

The *dielectric constant* (K_c) has its mechanical analog in the stiffness modulus. Most often it is measured as the ratio of the capacitance of a parallel-plate capacitor with the material as the dielectric compared to the capacitance of the same capacitor

in a vacuum—or air, which is about the same. The capacitance C_f in farads for a given plate spacing d in centimeters and plate area A in square centimeters is

$$C_f = \frac{K_c A}{d(3.6\pi 10^{-12})} \quad (10-3)$$

The capacitance is expressed in nano- (10^{-9}) or pico (10^{-12}) farads. Often the dielectric constant is measured in an alternating field. The reason more electrons can be stored on one plate of the capacitor at a given voltage with a solid dielectric is that electron fields in the material are distorted and counteract the impressed stress. Even a nonpolar polymer such as polyethylene can have valence electrons displaced to give an electronic displacement with a corresponding component of dielectric constant of about 2.0 to 2.5. A polar polymer such as poly(vinyl chloride), $(-\text{CH}_2-\text{CHCl}-)$, also can respond to an imposed field by actual orientation of molecular segments provided it is above T_g .

The *dissipation factor*, $\tan \delta$, is a measure of the hysteresis in charging and discharging a dielectric. One method of measuring it is in a Schering bridge circuit (Fig. 10-3) [9]. When resistance R_3 and capacitance C_{f_4} are adjusted to give a null at the galvanometer, the equivalent series capacitance of the specimen C_{f_1} is

$$C_{f_1} = C_{f_2} \frac{R_4}{R_3} \quad (10-4)$$

$$\text{and } \tan \delta = 2\pi\omega_c C_{f_4} R_4 \quad (10-5)$$

where ω_c is the frequency, C_{f_4} is in farads, and R_4 is in ohms. Since C_{f_2} and R_4 are usually fixed, adjustment of two dials gives a null and the dial for R_3 can be calibrated directly in capacitance, while that for C_{f_4} can be calibrated directly in dissipation factor. The power factor, $\sin \delta$, is sometimes specified, as is the loss factor, $K_c \tan \delta$. The power factor is the ratio of energy loss in a dielectric to the volt-ampere input.

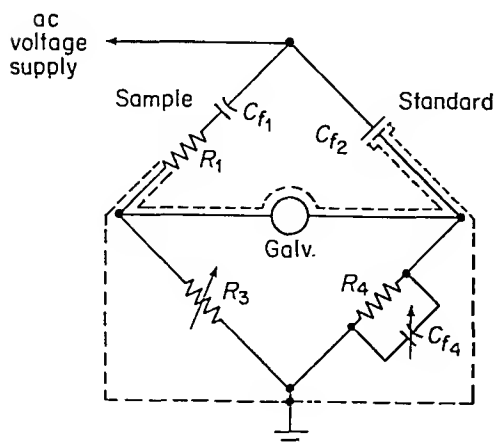


FIGURE 10-3
Simplified Schering bridge [9].

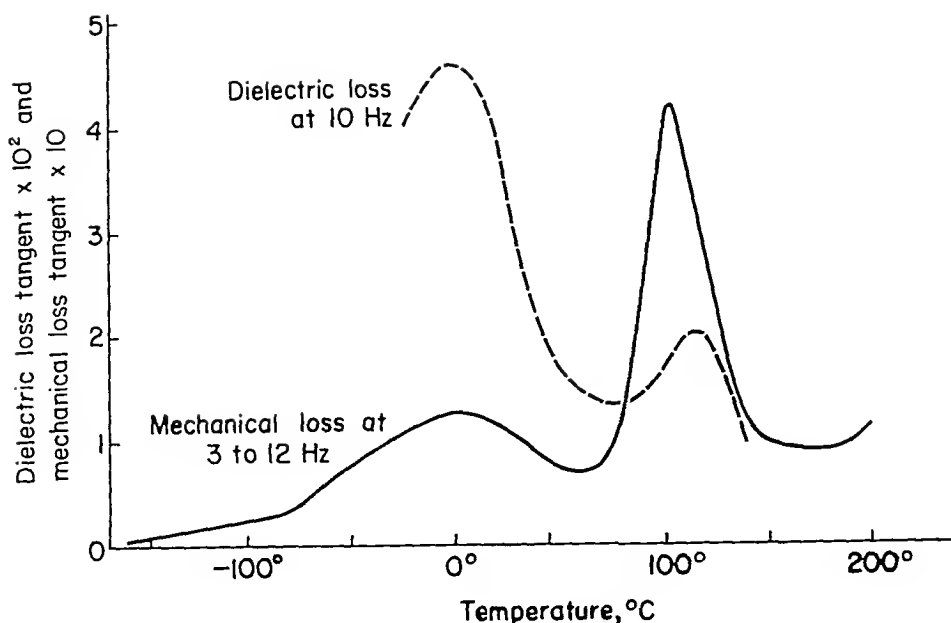


FIGURE 10-4

Mechanical and dielectric loss tangents for poly(chlorotrifluoroethylene). (After Saito *et al.* [11].)

Since the energy loss in a dielectric appears as heat, placing the material in a high-frequency field represents a method of heating a thick section uniformly. This is especially useful, because heat conduction is so poor that bringing a thick piece to a high temperature in an oven might take hours. The relationship between material properties, sample dimensions, and heating source parameters is [10]

$$U_p = 1.77 \times 10^{-13} \pi \omega_c K_c \varepsilon^2 A (\tan \delta) d^{-1} = 10^3 M c_p \frac{dT}{dt} \quad (10-6)$$

where U_p = power, watts

ω_c = frequency, Hz (cycles/s)

A = area, cm^2

K_c = dielectric constant

ε = voltage, rms volts

$\tan \delta$ = dissipation factor

d = sample thickness, cm

M = sample mass, kg

c_p = specific heat, $\text{J/g} \cdot ^\circ\text{C}$

dT/dt = rate of heating, $^\circ\text{C/s}$

Example Given the following information, find dT/dt and U_p .

Source parameters: $\omega_c = 10^6$ Hz, $\varepsilon = 10^4$ volts

Sample properties: $K_c = 3.0$, $\tan \delta = 0.035$, $c_p = 1.67 \text{ J/g} \cdot ^\circ\text{C}$

Density = 0.96 g/cm^3

Sample dimensions: $A = 1610 \text{ cm}^2$, $d = 2.54 \text{ cm}$

Solution $U_p = 3.7 \text{ kW}$, $dT/dt = 0.56^\circ\text{C/s}$. Actual expected dT/dt would be about 0.40°C/s .

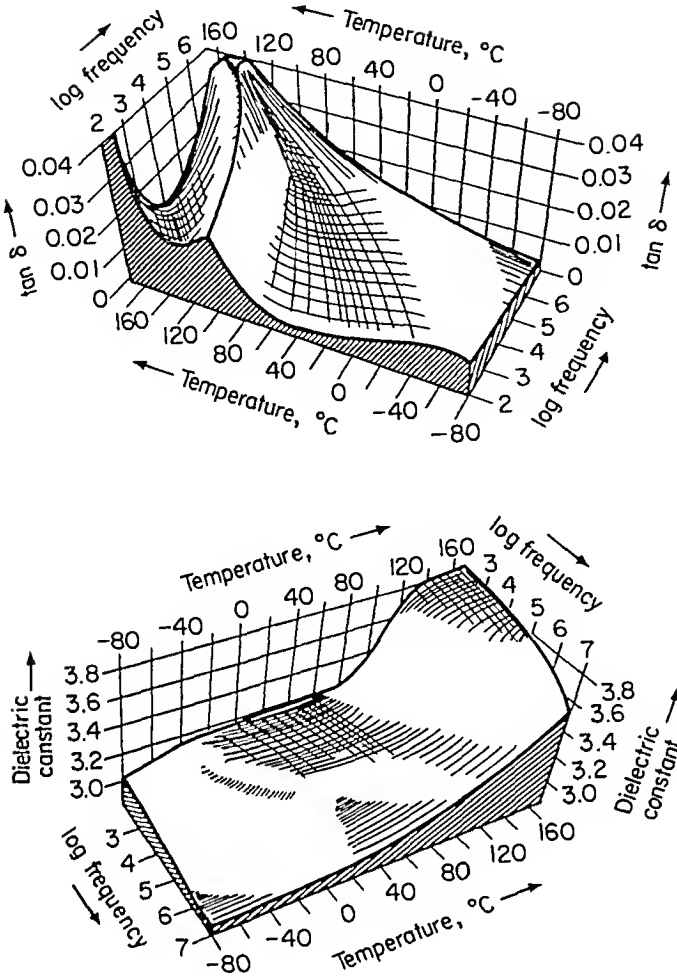


FIGURE 10-5
Dielectric constant and loss tangent as functions of frequency and temperature for poly(ethylene terephthalate) [12].

When a signal in the radio-frequency range is to be transmitted over long distances in coaxial cables, the dielectric loss becomes particularly objectionable.

The maxima in dielectric loss often parallel the maxima in mechanical loss for the same material. We expect maximum losses at transition temperatures (Fig. 10-4) for both electrical and mechanical deformations. In Fig. 10-5 we can see the increase

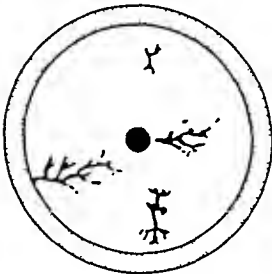


FIGURE 10-6
Treeing in a high-voltage cable [13].

in apparent main T_g (about 120°C) with increased frequency in the behavior of $\tan \delta$ for a partly crystalline material.

Just as mechanical fatigue after many alternating cycles causes a polymer to fail at a lower stress than in a rapid single test, so insulation can fatigue under electrical stresses. *Treeing* is a poorly understood phenomenon in which conductive paths extend themselves even at rather low overall voltages because the stress at the needlelike end of the tree is so high (Fig. 10-6).

PROBLEMS

- 10-1. A major concern of civic organizations and local governments has been the disposal of plastic containers. Bleach bottles and other blow-molded containers from polyolefins are lighter than water and litter the shores of our lakes and streams. What are some ways in which the problem might be attacked?
- 10-2. Polystyrene melt at 250°F is injected into a cavity in 0.4 min (compression rate of 10%/min) at 25,000 psi. What is the pressure after 10 min at constant volume and temperature? (Refer to Fig. 10-2.)
- 10-3. A silicone rubber cable is made with a conductive carbon-loaded core and an unfilled layer of insulation. If the resistivities are 10 and 10^{14} ohm $\cdot$ cm, respectively, and outer and inner diameters of the insulation are 0.3 and 0.1 cm, respectively, how fast will the cable heat up when a potential of 100 volts dc is impressed on a cable 10 m long? Assume the heat capacity of both filled and unfilled rubber to be $0.5 \text{ cal/cm}^3 \cdot ^\circ\text{C}$ and the cable to behave adiabatically.
- 10-4. If carbon black costs $\$0.30/\text{lb}$, oil $\$0.15/\text{lb}$, and EPDM rubber $\$0.95/\text{lb}$, what is the most economical composition (based on Fig. 10-1) that will yield a tensile strength of 1500 psi with a hardness of at least 50 (Shore A)? The carbon black has a density of 1.80 g/cm^3 , the oil of 0.92 g/cm^3 , and the rubber of 0.86 g/cm^3 .
- 10-5. A wheel is cast from low-molecular-weight polystyrene in a stainless-steel mold at 300°F . If the mold is 5 in in diameter at 75°F , what is the diameter of the plastic wheel at 75°F ? If the polymer had been molded under pressure to pack more material in the mold (see Fig. 10-2c), what pressure would have been needed to make the plastic wheel the same diameter as the mold at 75°F ? Linear coefficients of thermal expansion are $1 \times 10^{-5} (^\circ\text{F})^{-1}$ for steel and $1.5 \times 10^{-4} (^\circ\text{F})^{-1}$ for the polymer.
- 10-6. A cubic container with a volume of 1.00 m^3 is to be insulated so that a charge of 100 kg of ice will take at least 20 h to melt completely. What thickness of insulation is required? Urethane foam insulation, $k = 0.050 \text{ W/m} \cdot ^\circ\text{C}$; heat of fusion for water is 79.7 cal/g (334 kJ/kg); average outside temperature is 40°C .
- 10-7. The thermal resistance of pipe insulation can be calculated from Eq. (10-2) if the reciprocal of the thermal conductivity of the insulation is taken as the equivalent of the electrical resistance. The rate of energy loss from the pipe then is directly proportional to the temperature difference and inversely proportional to the thermal "resistance." If a 6.0-cm diameter pipe carries chilled water at an average velocity of 3.0 m/s over a distance of 1.50 km, what thickness of insulation (same k as in last problem) is needed to keep the temperature from rising more than 2.0°C when the inside temperature is 10°C and the outside is 65°C ? Neglect all resistance except that of the insulation.

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DEGRADATION AND STABILIZATION OF POLYMER SYSTEMS

Degradation is any undesirable change in properties that occurs after a material has been put into service. We can categorize degradation as affecting the polymer chemically or the polymer system physically or chemically. Examples of the latter would include the wearing of tires, the loss of plasticizer from a polymer system by evaporation or migration, or the separation of polymer from rigid fillers leaving voids at the interface. To counteract the degradation of systems by various agencies, certain *stabilizers* can be added that interfere with specific reactions. In this section we shall consider the agencies that produce degradation, the physical and chemical consequences of degradation, and some of the preventative measures that can be taken to diminish degradation.

11-1 DEGRADING AGENCIES

The agencies that bring about changes in polymers seldom act individually except in the laboratory. We can speak about the separate effects of heat, radiation, chemicals, and mechanical energy, but in practice, all four may be present to some degree. *Weathering* is a term used for outdoor exposure. During weathering, sunlight causes damage by ultraviolet radiation absorption as well as by heat built up by infrared absorption. Atmospheric oxygen and moisture provide the most common chemical attacks. And, of course, a sample may be mounted in a strained condition to approximate a real application.

In the laboratory the degrading agencies are usually separated. However, in some accelerated weathering tests a high-intensity mercury or xenon arc, water spray, and temperature and humidity control may be used. Outdoor exposure itself varies considerably from one location to another. Samples may be sent to Florida for sunlight and salt spray exposure and to Los Angeles for the effects of smog and ozone.

The spectrum of electromagnetic waves ranges from radio waves of long wavelength λ and low frequency ω_c to gamma rays (and cosmic rays) of short wavelength (Fig. 11-1).

The energy associated with a quantum or photon (the smallest unit of radiant energy) is simply related to the wavelength or frequency through Planck's constant h and the velocity of light c . Some interrelations are

$$\lambda \omega_c = c = 3.00 \times 10^8 \text{ m/s} \quad (11-1)$$

$$\frac{\text{Energy}}{\omega_c} = h = 6.62 \times 10^{-34} \text{ J}\cdot\text{s} \quad (11-2)$$

For example, light with a wavelength of 100 nm has a frequency of 3.0×10^{15} Hz. Knowing that 4.186 J equals 1 cal, and that there are 6.02×10^{23} molecules in a mole, we can calculate that the energy associated with this same radiation is 286 kcal/einstein. (The energy associated with 6.02×10^{23} photons is called an einstein.)

It can be seen from the distribution curve for the spectral energy of sunlight (Fig. 11-2) that most of the energy is in the visible region 380 to 800 nm. At the high-energy end, about $\lambda = 350$ nm, the energy per einstein is approaching or exceeding the dissociation energy of a number of covalent bonds found in polymers (see Sec. 2-1). Of course, the incident light may be transmitted, refracted, or scattered.

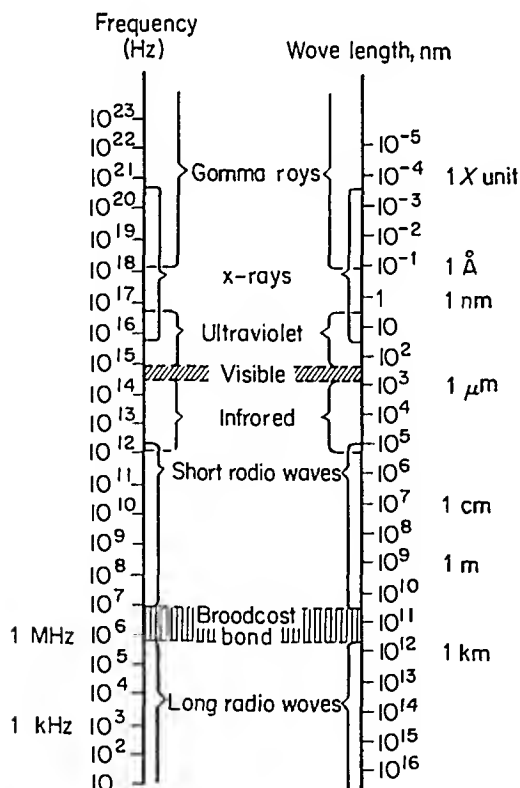


FIGURE 11-1

Chart of the electromagnetic spectrum. One Hertz is one cycle per second [1].

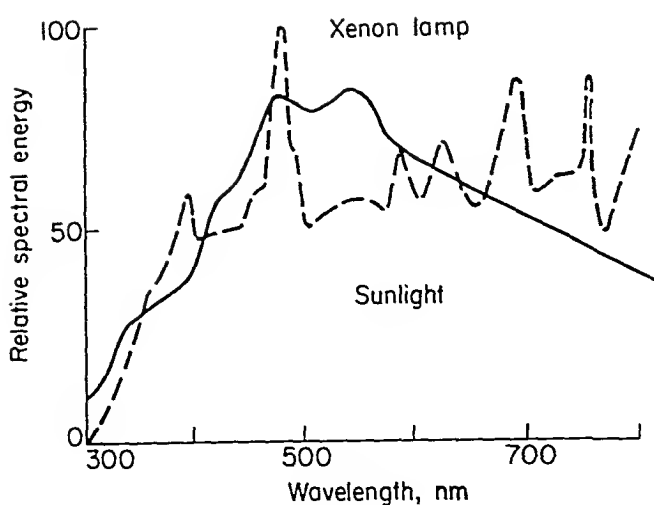


FIGURE 11-2
Spectral energy distribution [2].

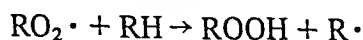
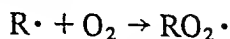
However, if it is absorbed locally in a polymer, dissociation may result, most commonly with the loss of a hydrogen atom, leaving a free radical on the chain. When ultraviolet light or gamma radiation is used, such dissociations become much more probable. The penetrating depth also increases with increasing frequency. At the other end of the sun's spectrum the infrared rays may be absorbed with no great localized energy but with a general increase in temperature. In the laboratory sunlight may be simulated by a xenon lamp having the spectrum shown in Fig. 11-2.

Almost all materials are subject to attack by oxygen and by water when they are put into use. The process of oxidation is so important that it is worth noting a few generalizations that have been made concerning it. Oxidation typically is a chain process [3]:

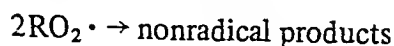
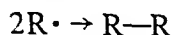
Initiation:

Production of $R\cdot$ or $RO_2\cdot$

Propagation:



Termination:



The end products are seen to consist of covalent carbon-carbon bonds, peroxide bonds, and perhaps hydroperoxides. Although any carbon-hydrogen bond might be

attacked, positions that are especially vulnerable are those adjacent to a double bond, adjacent to an ether linkage, or on a tertiary carbon (indicated by arrows in Table 11-1).

In the laboratory, the effects of oxidation are measured by several kinds of test. Most commonly, samples of a polymer system are aged at an elevated temperature in nitrogen, air, or oxygen. For air, a circulating air oven is used. Exposure to atmospheres of pure nitrogen or oxygen is usually carried out in sealed tubes (bombs). Changes in structure may be inferred from changes in physical properties such as tensile modulus or elongation at break on aging. A more sophisticated measure of change would be found in infrared spectral analysis. An actual measurement of the amount of oxygen absorbed is useful in studying the mechanism of oxidation. The four stages of oxidation found by Shelton and coworkers are shown in Fig. 11-3 [4]. The first two stages may not always be discernible in uninhibited polymers. In addition, one can measure the concentration of specific groups as a function of time or oxygen content (Fig. 11-4).

Moisture can be important by acting as a plasticizer or by acting as a solvent for some catalytic species. Ultraviolet light and oxygen usually will have different effects on a polymer depending on the humidity. This is especially true when the polymer has a substantial equilibrium moisture content. Nylon, for example, may vary in moisture content from 0 to over 5% depending on the humidity. Polyethylene

TABLE 11-1
Relative Rates of Oxidation Versus
Structure [3]

Structure	Relative rate of oxidation
$\begin{array}{c} \text{CH}_3 \\ \\ \text{-(CH}_2\text{)-C=CH-CH}_2\text{-} \\ \uparrow \qquad \qquad \uparrow \end{array}$	10
$\begin{array}{c} \text{CH}_3 \\ \\ \text{-(CH}_2\text{-CH-O-)} \\ \uparrow \end{array}$	9
$\begin{array}{c} \text{CH}_3 \\ \\ \text{-(CH}_2\text{-CH-)} \\ \uparrow \end{array}$	6.5
$\begin{array}{c} \text{CH}_3 \\ \\ \text{O} \\ \\ \text{-(CH}_2\text{-CH-)} \\ \uparrow \end{array}$	2.8
$\begin{array}{c} \text{CH}_3\text{CH}_2\text{-O} \\ \\ \text{C=O} \\ \\ \text{---CH}_2\text{-CH---} \\ \uparrow \end{array}$	1.4

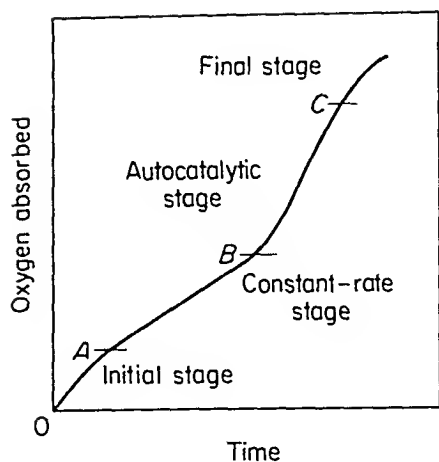


FIGURE 11-3

Four stages observed in oxygen-absorption measurements on elastomers [4].

has almost no moisture content. Water penetration at the interface between two phases can cause delamination. The hydroxyl-rich surface of glass has a great affinity for water, so that a layer of organic polymer on the glass may be displaced by water at high humidities. Another reaction with water is hydrolysis. In some of the first commercial urethane foams (1950s) it was found that the urea, urethane, and aliphatic ester groups were rather easily hydrolyzed, the rate increasing with pH above 7. Present-day formulations are much less sensitive. But water remains a factor to be considered whenever hydrolyzable groups are part of the polymeric structure.

The overall view of chemical attack is impossible to condense because of the wide variety of chemical species and polymeric substrates. Whenever a polymer is suggested as a material of construction in a chemical plant, a thorough consideration

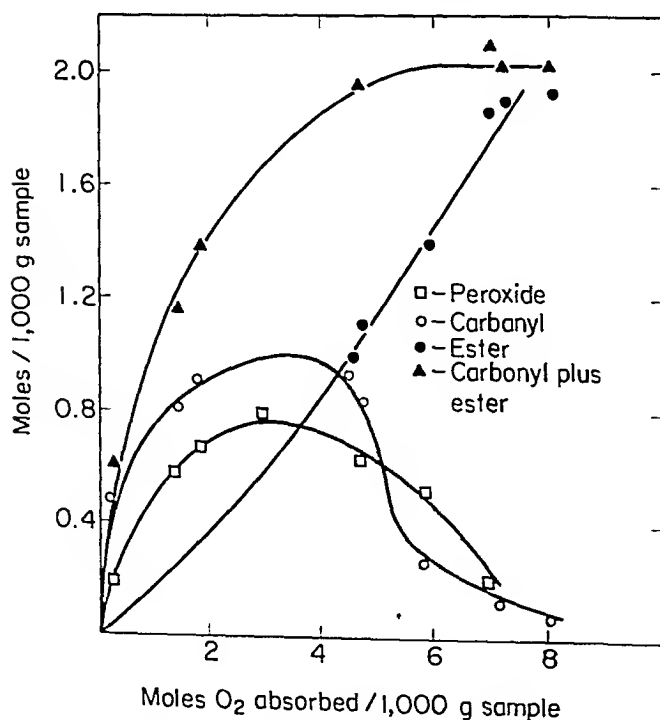


FIGURE 11-4

Concentration of peroxide, carbonyl, and ester groups as a function of oxygen absorbed in oxidation of 5-phenyl-2-pentene at 80°C [4].

of resistance to specific chemicals is desirable. Polymeric pipes and tank liners are used for acid and alkali, oxidizing and reducing agents, and all kinds of organic reactants. In each case the most economical solution will be specific, because factors of initial cost, versatility, and maintenance may enter in.

Biological attack includes alteration of polymer systems by fungi, bacteria, and larger species such as insects and animals [5-7]. Most naturally occurring polymers are biodegradable in their native state. Cellulose and natural rubber can be digested by a variety of microorganisms. Modified natural materials such as acetylated cellulose or sulfur-cross-linked rubber are quite resistant. Totally synthetic polymers, by and large, are resistant to attack when the molecular weight exceeds about 5000. Some heterochain polymers, including polyesters, polyamides, and polyurethanes, may degrade in the presence of some microorganisms [5, 8]. In this degradation the microorganisms are using the material as a source of nutriment, with enzymes generated by the organism acting as catalysts. For many years the polymer industries emphasized the development of bioresistant materials. The treatment of cellulose to prevent deterioration of cotton and linen in tropical climates has long been a major effort of military suppliers. Since the early 1970s public concern for the problem of litter as part of the overall problem of waste disposal has led to development of polymers that are biodegradable. However, the cost and the health hazard of marketing polymer containers that are truly biodegradable has outweighed the esthetic advantages they might have. Waste disposal is discussed also in Sec. 11-7.

Purely mechanical agencies can include the effect of solvents on the macroscopic dimensions of a material. Swelling of rubbers and melts was mentioned in Sec. 2-5 in connection with cohesive energy density. Solvents may extract portions of polymer systems, e.g., the plasticizer from a poly(vinyl chloride)-based system. Swelling at a surface may set up a stress that is relieved by *crazing*. Craze lines consist of oriented polymer. They become evident by their opacity in glassy polymers stressed by a purely mechanical couple or by surface absorption of a liquid (see Sec. 9-7).

High-speed stirring, turbulent flow, and ultrasonic irradiation of polymer solutions can cause changes in polymer structure. The predominant response is a decrease in molecular weight, because recombination of radicals is not favored in solution. When a melt is masticated at high shear rates, a great deal of mechanical energy is dissipated in the system. Recombination of radicals can take place, as well as some other reactions depending on circumstances.

11-2 PHASE SEPARATION AND INTERFACIAL FAILURE

The degradation of a polymer system can take place without changing the structure of the whole polymer. The two common cases are where one component of a homogeneous mixture is extracted and where components of a heterogeneous assembly delaminate.

The extraction of plasticizer from a poly(vinyl chloride) composition does not always require organic solvents. Soapy water in contact long enough with a foam or film can extract low-molecular-weight plasticizers. A plasticized vinyl shower curtain has the added hazard of relatively high temperatures and humidities to contend with.

When a plasticized system is put in physical contact with an unplasticized polymer, the plasticizer may *migrate* from one to the other. In designing a vinyl coaster, for example, the compounder must take into account the possibility that the item may be placed on a lacquered surface. Migration of dioctyl phthalate from the poly(vinyl chloride) coaster to a cellulose acetate surface will result in a softened, marred appearance.

Delamination is most easily illustrated by interior plywood soaked in water. The layers may come apart as the wood swells and the phenolic adhesive is displaced. The same sort of failure can occur in a glass-fiber-reinforced thermoset. Coupling agents that tie glass and polymer together can decrease this tendency (see Sec. 9-8). Systems that delaminate are not always so obviously heterogeneous to start. It is common for large injections of molded polyethylene objects to develop a layer that peels off in the vicinity of the injection point on aging. Apparently the crystal structure of the polymer that first enters the cold cavity and coats the wall is different from the structure developed by subsequent polymer cooled more slowly. The interface between the two represents a plane of weakness that is aggravated by warm water and detergent. A continued change in crystalline structure at the interface may be taking place.

Mechanical stresses often induce delamination. A tensile stress in loaded rubber may tear polymer from filler, leaving vacuoles (Sec. 9-8). Constant flexing of a conveyor belt or a tire may pull rubber from the fibrous reinforcement.

11-3 POLYMER DEGRADATION

As far as the polymers themselves are concerned, many types of "degradation" can be predicted from the reactions of low-molecular-weight analogs. Oxidation of hydrocarbons and hydrolysis of esters are often more easily studied in such analogs. However, as we consider the response of polymers that are predominantly linear, we can categorize degradation as affecting the backbone of the polymer or the side chains on the polymer. Some degradative effects are:

- | | |
|-----------------------|--------------------|
| 1. Scission | } Backbone effects |
| 2. Depolymerization | |
| 3. Cross-linking | |
| 4. Bond changes | |
| 5. Side-group changes | |

In *chain scission* we have bonds broken at random within the polymer molecules. Each breaking bond creates another molecule and lowers the average molecular weight. Hydrolysis of a polyester is a good example of a *random scission* process, since the susceptibility of a bond does not depend greatly on molecular size. If we take a polyester of number-average degree of polymerization $\bar{x}_n$ in a dilute solution of concentration c (g/dl), we can calculate the concentration of ester bonds in the system $[\phi]$:

$$[\phi] = (N, \text{concentration of monomer units in solution}) \\ - (m, \text{concentration of polymer molecules})$$

$$[\phi] = N - m \quad (11-3)$$

$$N = \frac{c}{M_0} \quad (11-4)$$

$$m = \frac{N}{x_n} \quad (11-5)$$

where M_0 is the molecular weight of a monomer unit.

If we postulate that the rate of bond disappearance (hydrolysis) with time ($-d[\phi]/dt$) will be proportional to the bond concentration $[\phi]$, we have a first-order expression

$$-\frac{d[\phi]}{dt} = k[\phi] = k(N - m) = \frac{kc(1 - 1/x_n)}{M_0} \quad (11-6)$$

Also, differentiating the second and fourth terms of Eq. (11-6) yields

$$-k \frac{d[\phi]}{dt} = \frac{kc}{M_0} \frac{d(1/x_n)}{dt} \quad (11-7)$$

But in Eq. (11-6), $1/x_n \ll 1$; therefore, the reaction is "pseudo-zero-order" and

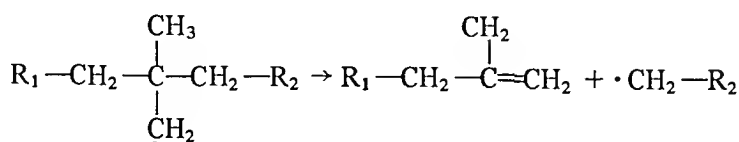
$$\frac{c}{M_0} \frac{d(1/x_n)}{dt} = \frac{kc(1 - 1/x_n)}{M_0} = \frac{kc}{M_0} \quad (11-8)$$

If we start at time $t = 0$ and $x_n = (x_n)_0$, we get the change in number-average degree of polymerization as a function of time.

$$\frac{1}{x_n} - \left(\frac{1}{x_n}\right)_0 = kt \quad (11-9)$$

It should be emphasized that this relationship holds only when $x_n \gg 1$. When $(x_n)_0 = 1000$, for example, breaking one bond in each molecule cuts x_n to 500. However, the available number of hydrolyzable bonds has been decreased by only 0.1%.

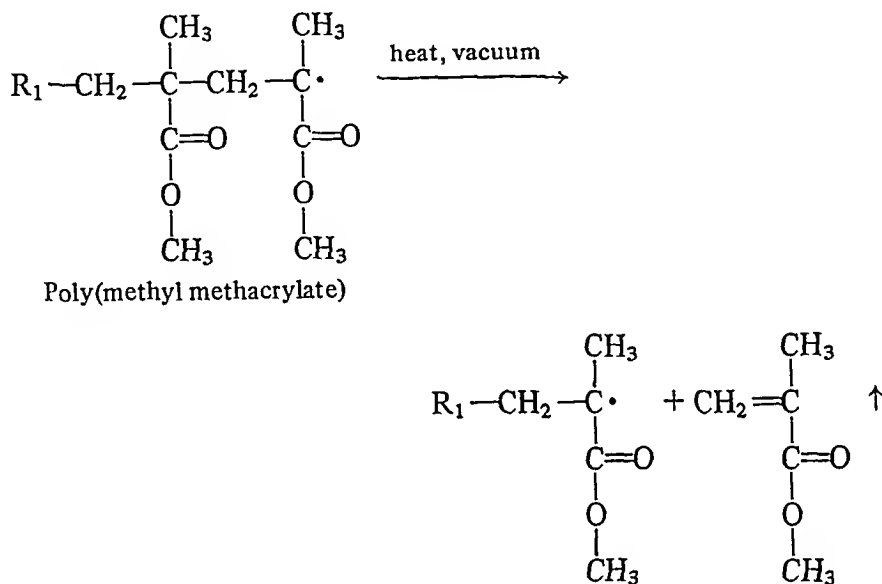
Polymers containing a completely substituted carbon in the chain often undergo chain scission on oxidation or exposure to ultraviolet or gamma radiation. This is because rearrangements are formed when an unpaired electron is left on a structure as in polyisobutylene:



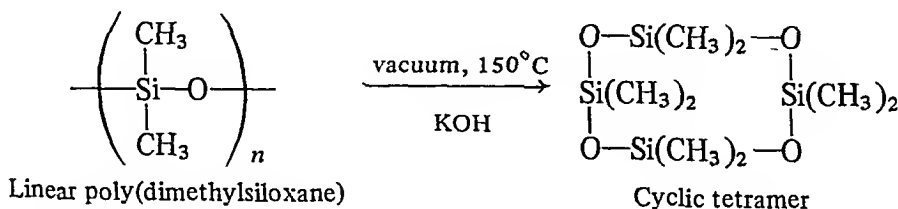
Some other structures that favor chain scission are polypropylene, polyacrylates, and polymethacrylates. Because the industrially important process of cross-linking rubber

often is carried out under oxidative conditions, and because chain scission generally is undesirable, other agencies must be employed for cross-linking when the chain contains such unstable groups.

Depolymerization also decreases molecular weight. Some common examples are merely the polymerization reactions previously considered taken in reverse. With some systems, almost quantitative regeneration of monomer is possible. In fact, depolymerization is used to recover monomers from scrap polymer when economics permit. For example, methyl methacrylate can be recovered in good yield and in high purity from the polymer by using low pressures, high temperatures, and a source of free radicals:

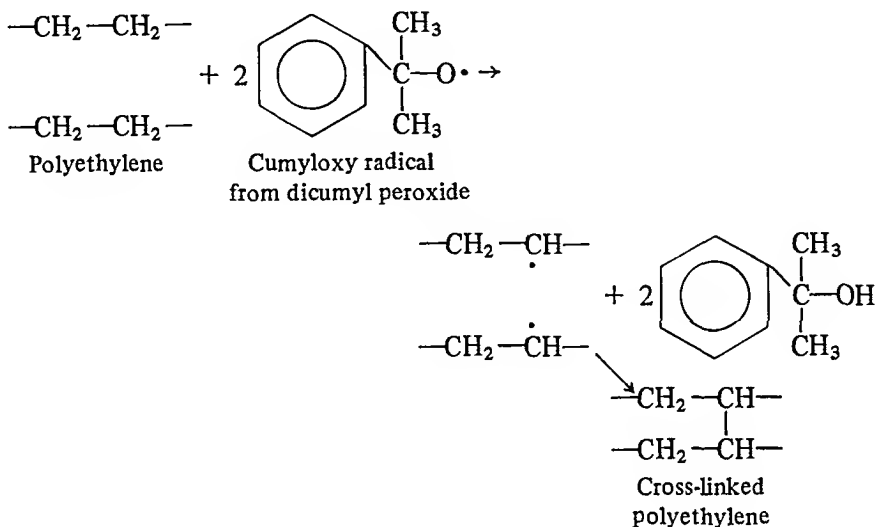


Polystyrene also depolymerizes under these conditions, but the original monomer is not expensive enough to warrant commercial regeneration from scrap polymer. Ionic reactions also may lead to depolymerization. Heating almost any polysiloxane with potassium hydroxide in a vacuum eventually will convert the entire system to volatile cyclic material, predominantly the eight-membered ring of the tetramer:



Although cross-linking is a useful reaction in making a rubbery material that is dimensionally stable at high temperatures, there may be undesirable consequences when it occurs after a material is in service. The modulus increases with cross-linking, but the energy-absorbing capacity goes through a maximum and decreases thereafter. A rubbery polymer system generally becomes brittle as a result. Another typical pattern accompanying cross-linking is a decrease in compatibility, so that plasticizers exude, systems shrink, and delamination occurs. Polyethylene affords a primitive

example of desirable and undesirable cross-linking. Molten polymer (150°C) may be mixed with a peroxide that does not decompose until an even higher "curing" temperature (205°C) is reached. The finished product is a cross-linked polymer very useful as high-temperature electrical insulation. Cross-linking can also be induced by gamma radiation or high-energy electron beams:



However, the same polyethylene in film form outdoors may undergo slow attack from atmospheric oxygen in the presence of sunlight. Although cross-linking does take place, it is accompanied now by incorporation of oxygen to give polar groups and by chain scission. The end result is a brittle, easily ripped film with poor optical and electrical properties.

Accelerated aging tests have been mentioned in an earlier discussion of oxidation. It is desirable in analyzing such tests to be able to measure cross-linking and chain scission. For rubbery polymers this can be done by making two kinds of measurements [9]. Both depend on the proportionality of cross-link density with modulus (see Sec. 8-2). It should be obvious that if a tensile modulus E_t is measured intermittently on an aging sample, any cross-link that is formed will be reflected in an increased modulus. Chain scission, on the other hand, will decrease this modulus. In other words, the rate of change of E_t is the difference in the rates of cross-linking (dN_c/dt) and chain breaking (dN_s/dt):

$$\frac{dE_t}{dt} = K \left(\frac{dN_c}{dt} - \frac{dN_s}{dt} \right) \quad (11-10)$$

where K is a proportionality constant.

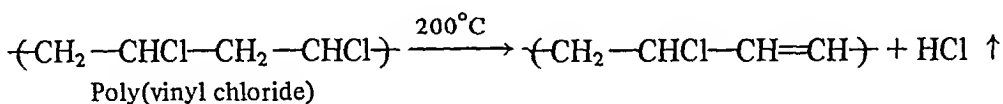
Now in a separate test we can measure the relaxation of stress in a sample held at constant elongation. Any chain scission that occurs also decreases this relaxation modulus E_r . However, cross-linking of the strained sample does not increase the modulus, because only the cross-links that were put in the relaxed sample and were distorted from their equilibrium, random positions will contribute. For this case, we measure only the rate of chain breaking:

$$\frac{dE_r}{dt} = -K \frac{dN_s}{dt} \quad (11-11)$$

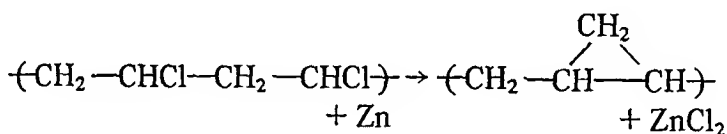
where K is the same constant as in Eq. (11-10).

The simultaneous measurement of E_t and E_r for polybutadiene aged in air at 130°C can be interpreted as showing that much scission and limited cross-linking occurs up to 1 h (Fig. 11-5). After 10 h the main reaction is cross-linking, and chain scission almost ceases.

Changes can be wrought in the polymer backbone without scission or cross-linking. When poly(vinyl chloride) is heated above 200°C in the absence of stabilizing materials, copious quantities of HCl are evolved after a few minutes. Although scission and cross-linking ensue, the primary effect of heating this polymer is dehydrohalogenation, which



changes the backbone structure. The allyl chloride structure that is left after a single abstraction of HCl is more susceptible to free-radical attack than the fully saturated material. A "zippering" occurs, leaving behind successive conjugated double bonds. This remaining structure is chromophoric and highly reactive with metal salts and with oxygen. Since the chain cannot rotate around double bonds, it is stiffened even in the absence of cross-linking. Other reactions can take place that alter the backbone stiffness. When heated in zinc metal powder, poly(vinyl chloride) can be cyclicized to a large extent:



As with most degradation reactions, these changes in structure are sometimes channeled into useful applications. For example, the induction period for dehydrohalogenation in the presence of zinc oxide is decreased by exposure to ultraviolet light. A photograph can be reproduced using degraded polymer as the chromophores by "heat

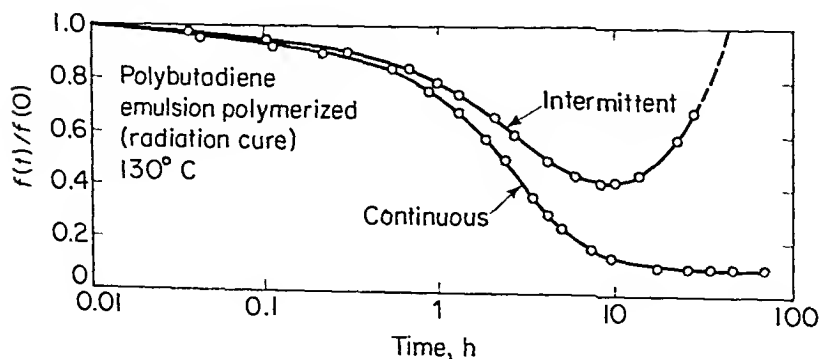
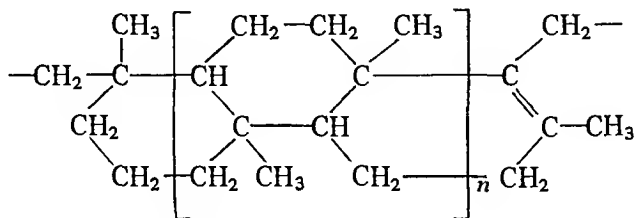


FIGURE 11-5

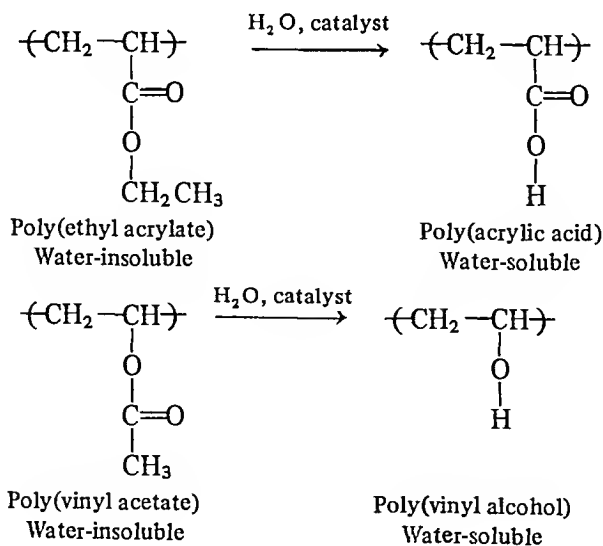
Continuous stress-relaxation and intermittent stress measurements at 130°C [9].

developing" the latent image from light exposure of such a system. The exposed areas darken first on heating. A rather good halftone image can be reproduced, although the film speed is quite slow [10].

The oxidation of polyacrylonitrile to give a heat-stable, ladder polymer was mentioned in Sec. 3-5. Natural rubber is cyclicized in order to give abrasion-resistant ink and paint resins. In the presence of chlorostannic acid ($\text{H}_2\text{SnCl}_6 \cdot 6\text{H}_2\text{O}$), *cis*-polyisoprene is cyclicized by refluxing in benzene. The new material can be reduced to a powder at room temperature, indicating that its T_g has been raised considerably over the original -70°C . Cross-linking and chain scissions have not taken place to any large extent, since the product redissolves completely to give solutions of high viscosity. The probable structure is [11]:



Of course, reactions of the "foliage," the side chains on polymers, can take place without altering the molecular weight or the chain stiffness. Changes in solubility, compatibility, color, and mechanical and electrical properties may result. The main chains of poly(ethyl acrylate) or poly(vinyl acetate), for example, are not affected by hydrolysis. But in either case, hydrolysis changes the water-insoluble precursors into water-soluble resins:



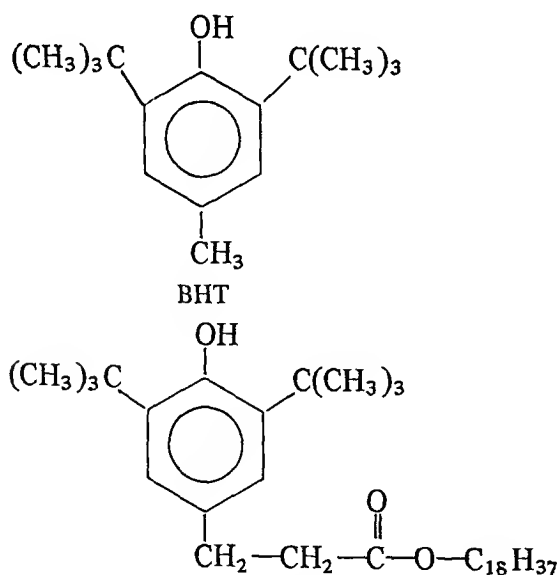
In the case of poly(vinyl alcohol), the reaction is a commercially useful one. But in either case, a drastic change in solubility has been made. It is clearly an undesirable change if the precursors are being used as water-insoluble protective coatings.

11-4 ANTIOXIDANTS AND RELATED COMPOUNDS

The most frequently employed stabilizing ingredient in plastics, fibers, rubbers, and adhesives is the antioxidant. Since oxidation is a free-radical, chain process, it is to be expected that useful molecules will be those that combine with free radicals to give stable species incapable of further reaction.

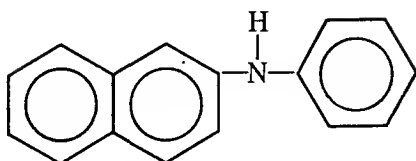
Quinones may act as free-radical stoppers by adding the radical to the ring or to the carbonyl oxygen. The most widely used classes of antioxidants are the hindered phenols and diaryl amines. Presumably these react with RO_2 radicals by giving up a hydrogen and forming a rather stable radical, which also might stop a second radical by combining with RO_2 . Electron transfer and ring-addition reactions may take place also. It will be recalled that such action may be thought of as *degradative chain transfer* and that it is the principle by which inhibitors of free-radical polymerization function (see Sec. 4-4). Two important considerations in selecting antioxidants can be toxicity and color formation. The use of any chemical additive in food wrapping must be approved by the appropriate federal agency (Food and Drug Administration). Usually, only specific formulations and not general classes of materials are approved. In stabilizing rubber, antioxidants are classified as staining or nonstaining depending on whether or not they develop color in use. In a carbon-black-loaded tire tread, a staining material is no drawback. But in the white sidewalls, it is important to use additives that are colorless to start with and stay colorless as they protect against oxidation.

A widely used antioxidant in food products is butylated hydroxytoluol (BHT):

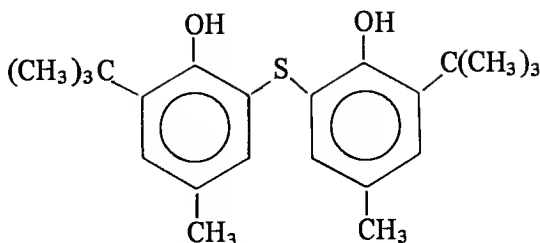


Fatty ester of hindered phenol

It is added to a variety of consumer items ranging from chewing gum and potato chips to bread wrapping and vitamin A. When modified as in the fatty derivative, an antioxidant of lower volatility and better compatibility with polyethylene is formed. Some antioxidants that have been used in rubber are phenyl- β -naphthyl amine (staining) and a sulfur cross-linked, hindered phenol (nonstaining):



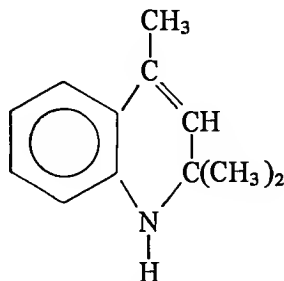
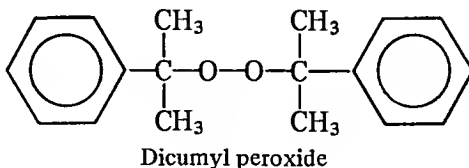
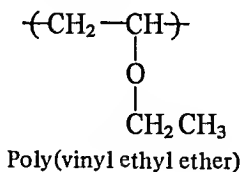
Phenyl- β -naphthyl amine
(PBNA), staining



2,2'-thiobis(4-methyl-6-*tert*-butyl
phenol), nonstaining

Most unsaturated raw rubber has a small amount of antioxidant added before shipping to protect it during storage. Butyl rubber may have only four double bonds for each 1000 single bonds in the main chain, but it is usually supplied with BHT (about 0.1%). Ethylene-propylene terpolymer has a higher level of unsaturation, but it is confined to pendant groups of somewhat lower reactivity. About 0.25% of BHT is added by one manufacturer.

In contrast to the small amounts of antioxidant in raw rubber, compounded rubber often contains several percent of protective material. It seems contradictory at first that antioxidants can continue to be very effective even after the polymer system has undergone a high-temperature, oxidative cross-linking. A case in point is poly(vinyl ethyl ether) cross-linked by dicumyl peroxide:



Trimethyl dihydroquinoline

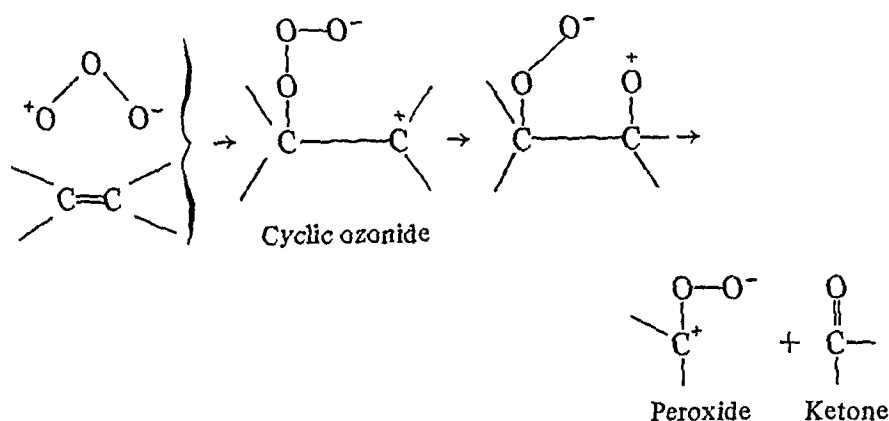
In a primitive formula the only ingredients besides the polymer are a reinforcing filler, a lubricant, and the cross-linking agent (Table 11-2). The cross-linking reaction takes 30 min at 150°C. Adding as much as two parts of antioxidant, Agerite Resin D, a

TABLE 11-2
Poly(Vinyl Ethyl Ether) Rubber [12]

Ingredient	Formulation, parts by wt
Polymer (Bakelite EDBM, Union Carbide)	100
Carbon black (Wyex, channel black, Huber)	50
Stearic acid	2
Dicumyl peroxide	4

polymerized trimethyl dihydroquinoline [13], does not degrade the original tensile strength or elongation. And yet the antioxidant is quite effective in preventing degradation for a period of a week in air at 120°C (Figs. 11-6 and 11-7).

Ozone (O_3) also attacks polymers. Unlike molecular oxygen (O_2), ozone appears to add directly to a double bond [14, 15]. Subsequently, chain scission often occurs. The circumstances generally calling for



stabilization against ozone are the combination of a highly unsaturated material, such as diene rubber (polyisoprene, styrene-butadiene rubber), some stress, and, of course, ozone. The automobile tire, especially in some urban locations, combines these features. Although the usual concentration of ozone in the atmosphere is only 0 to 20 parts/100 million, in the Los Angeles area it may run to about 25 parts/100 million (and can reach concentrations of 80 parts in heavy smog). An even higher concentration is encountered on the surface of high-voltage insulators. *Corona discharge* is the flow of electric energy from a high-voltage conductor through ionized air on the surface or in voids or air spaces between conductor and insulation. Although most corona testing is done at voltages of over 10,000 V, the discharge may commence at less than 1000 V. The discharge is accompanied by a faint glow (hence the name "corona") and a crackling sound indicating the pulsating character of the conduction. Oxygen is converted to ozone (ozone generators are built on the principle of corona discharge) so that an insulator may be subjected to very high concentrations.

In insulators the physical changes that are noted are pitting, erosion, and discoloration; and the chemical changes are chain scission and oxidation. In rubber for

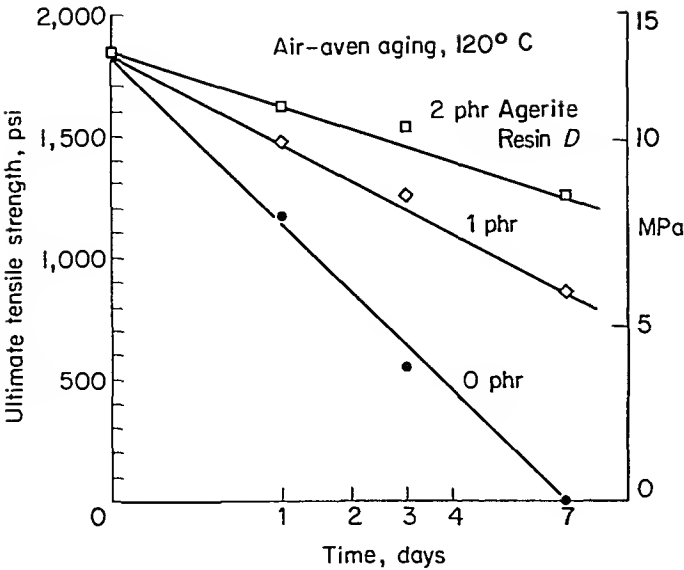


FIGURE 11-6
Effect of antioxidant (polymerized trimethyldihydroquinoline) on tensile strength of poly(vinyl ethyl ether) [12]. Abscissa is time^{1/2}.

tires most tests are run on static specimens at various strains. A sample elongated 20% cracks much more rapidly than an unstrained sample. The sensitivity does not continue to increase with elongation but may go through a maximum. The particular manifestation usually studied is crack growth. Under a given set of conditions a crack, started by a razor blade will grow in linear fashion perpendicular to the direction of mechanical strain.

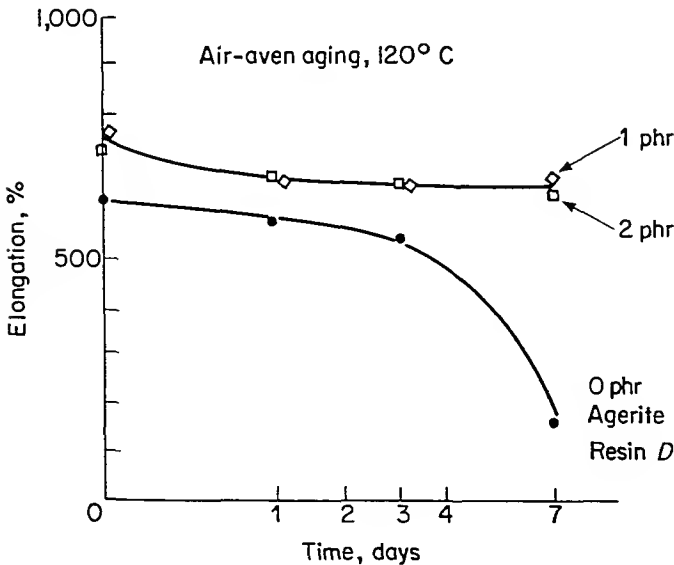


FIGURE 11-7
Effect of antioxidant on elongation at break for polymer of Fig. 11-6 and Table 11-2 [12].

Some antiozonants are effective just by forming a surface barrier to diffusion of O_3 . Waxes can be added that *bloom*, i.e., that exude to the surface, and form a sacrificial layer of hydrocarbon. Dialkyl-*p*-phenylenediamines (the largest chemical class) may react directly with ozone or with the ozone-olefin reaction products in such a way as to interfere with chain scission. Even the reaction products of this latter class may form an additional barrier to O_3 diffusion, since they react at the surface initially. It can be seen that addition of such an amine *increases* the rate of ozone absorption initially but affords protection after a short time (Fig. 11-8).

The proclivity of poly(vinyl chloride) toward dehydrohalogenation is shared to some extent by other chlorinated aliphatic materials including poly(vinylidene chloride), chlorinated waxes, and chlorosulfonated polyethylene. Since worldwide production of poly(vinyl chloride) exceeds 15×10^9 kg/year, the production of stabilizers to retard dehydrohalogenation is itself a multimillion-dollar business. The degradation reaction is not completely understood, although it has been studied extensively over a period of 40 years [16]. On a practical level, however, the species effective in stabilizing poly(vinyl chloride) typically are found to:

1. Absorb or neutralize HCl
2. Displace "active" chlorine atoms such as those on tertiary carbons
3. React with double bonds
4. React with free radicals
5. Neutralize other species that might accelerate degradation.

Metal soaps of barium, cadmium, lead, zinc, and calcium obviously can react with HCl. The addition of a zinc soap (or zinc oxide) to poly(vinyl chloride) gives a

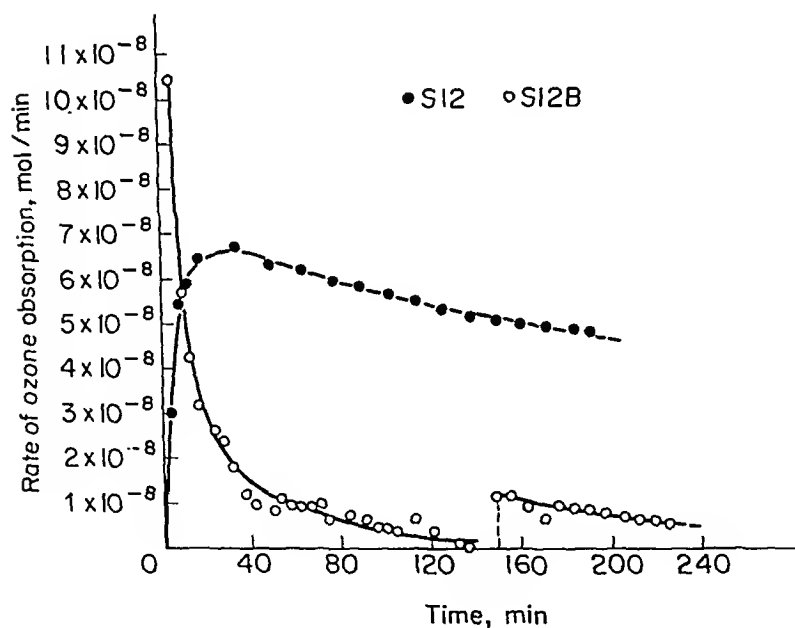


FIGURE 11-8

Rate of ozone absorption vs. time for a specimen under 20% elongation. Ozone flow rate = 1.05×10^{-7} mol/min. S12 is unprotected elastomer. S12B contains 2 phr of *N,N'*-di-*sec*-butyl-*p*-phenylenediamine [15]. The discontinuity in the curve for S12B resulted from an interruption in the test that allowed more ozone-sensitive material to diffuse to the surface.

material that can be heated at 175°C for 10 or 15 min with scarcely any discoloration, as opposed to a control with no zinc that turns yellow or brown as a result of the conjugated unsaturations and oxidized structures. However, once the zinc is converted in large measure to zinc chloride, there is a very rapid and copious evolution of HCl and the remaining material is blue-black and brittle. The zinc soap, which was a stabilizer, is converted to zinc chloride, a rapid and efficient degradation catalyst.

Besides the metal soaps and general antioxidants, some species used to stabilize poly(vinyl chloride) are organo-tin compounds, epoxy compounds, phosphites, and phenols.

11-5 STABILIZERS FOR IRRADIATED SYSTEMS

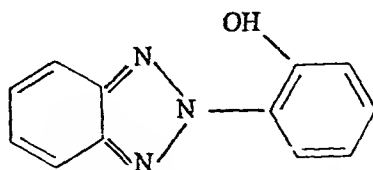
Most *UV-absorbers* protect the substrate by preferentially absorbing the harmful portion of the sun's spectrum between 300 and 400 nm. The earth's atmosphere filters out most of the shorter wavelengths. To be effective, the UV-absorber should dissipate the absorbed energy by transferring it to its surroundings as heat or by re-emitting it at longer wavelengths through phosphorescence, fluorescence, or infrared radiation. Some other desirable properties for a UV-absorber are compatibility with the substrate, lack of visible color, low vapor pressure, low reactivity with other materials in the system, and low toxicity.

Carbon black can be tolerated in a limited number of formulations where color is not a criterion. The pigment not only absorbs light, it is reactive with those free-radical species that might be formed. Wire and cable insulation and pipe for outdoor applications can be protected this way. Films for mulching and water containment in ponds may be made from polyethylene containing carbon black. Five UV-absorbers and their corresponding transmission curves are shown in Table 11-3 and Fig. 11-9. The common feature of these UV-absorbers is conjugated unsaturation enhanced by stable aryl groups. A variety of groups may be substituted on these basic structures in order to decrease solubility in water and volatility or to increase compatibility.

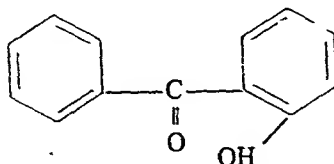
Phenyl salicylate has the common name "salol." In addition to its use as a stabilizer in polymers, salol is used at concentrations of about 1 to 10% in suntan oils and ointments, as are other absorbers. The function of the stabilizer in such a situation is the same as in the polymer, to decrease the concentration of skin-damaging radiation. Toxicity and reactivity take on a personal and obvious importance for this application. Suntan oils illustrate one way in which stabilizers can be used. If the UV-absorber is in a thin layer on the surface, the article is protected to a greater extent than if it is dispersed throughout. Occasionally this can be done as when multiple coats of lacquer are applied to furniture. All the UV-absorber can be put in the top coat. When articles are to be molded, however, it is not economical to coat separately, so the UV-absorber is mixed in with the other ingredients.

Despite the addition of stabilizers, many polymer systems reflect less visible light at short wavelengths (400 nm) than at long ones (700 nm). To compensate for this nonuniformity, a blue dye can be added that absorbs at long wavelengths but not at short ones. For years *laundry bluing* has been added to fabrics to give an overall whiteness. In doing this the total reflectance is decreased. *Brighteners*, also called *optical bleaches*, operate by absorbing invisible light below 400 nm and then fluorescing

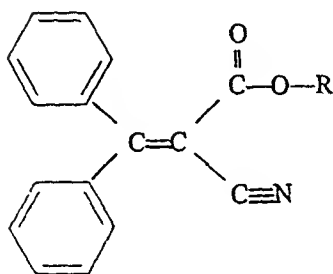
TABLE 11-3
Structures of Five Different UV-Absorbers [17]



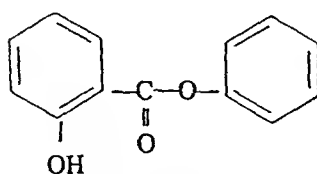
2-(Hydroxyphenyl)benzotriazole



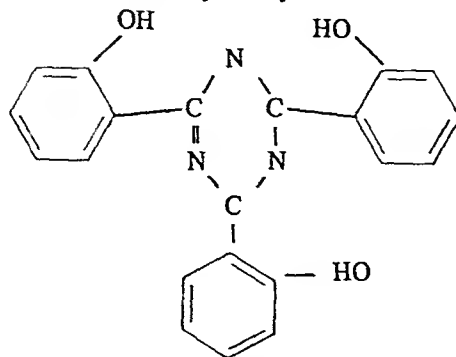
2-Hydroxybenzophenone



Alkyl-2-cyano-3-phenyl cinnamate
 (substituted acrylonitrile)



Phenyl salicylate



1,3,5-Tris(2'-hydroxyphenyl)triazine

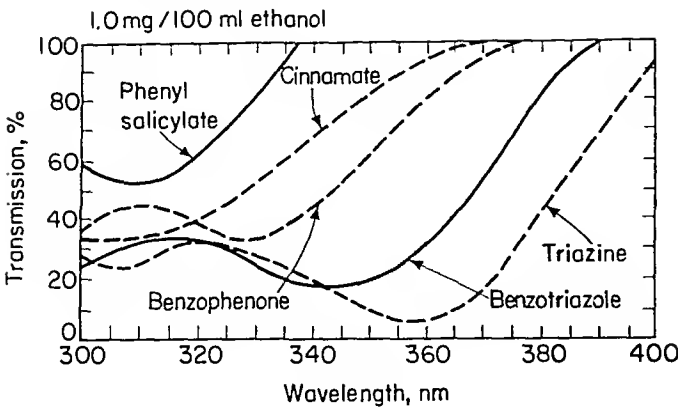
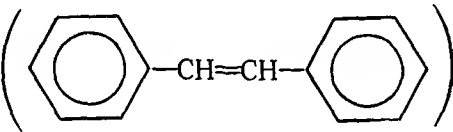


FIGURE 11-9
Transmission of ultraviolet light by absorbers listed in Table 11-3 [17].

in the visible wavelengths [18]. The effect is seen in Fig. 11-10. A violet dye decreases total reflectance in a poly(vinyl chloride) plaque. The fluorescent whitening agent absorbs light at less than 400 nm and reemits it between 400 and 500 nm. Some typical structures (Table 11-4) incorporate the stilbene group:



In Fig. 11-11, the absorption and emission spectra for structure 1 of Table 11-4 have been superimposed. Brighteners have been used in soaps and detergents extensively since 1948 and undoubtedly gave rise to the various extravagant advertising claims for whiteness with which the soap-consuming public has been bombarded ever since. Textile and paper usage of brighteners followed. Typical concentrations in plastics are of the order of 0.001 to 0.05%. Because the brighteners “feed” on ultraviolet light, their effect is most noticeable by sunlight and hardly perceptible by incandescent light. Fluorescent lights give an intermediate effect. Also, more brightener has

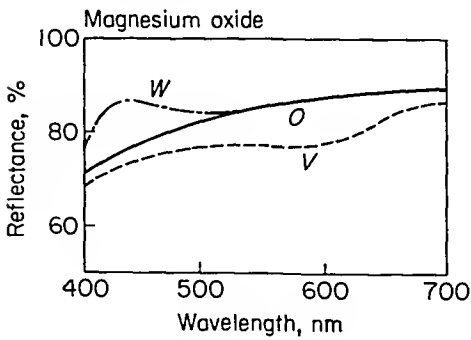
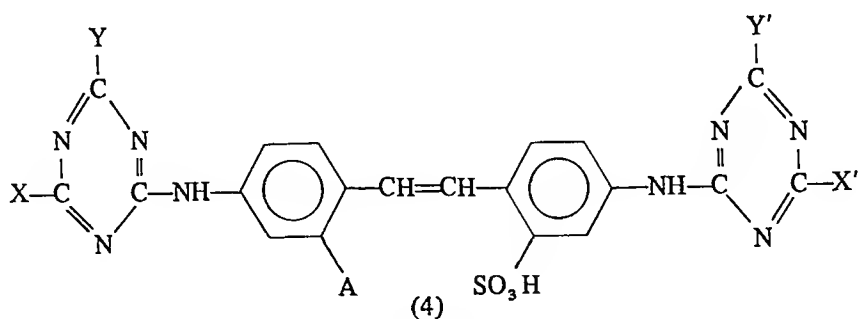
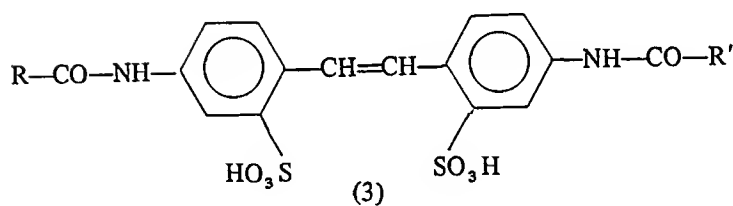
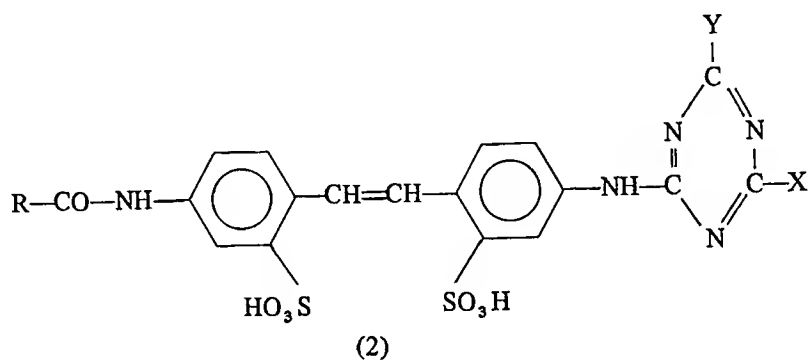
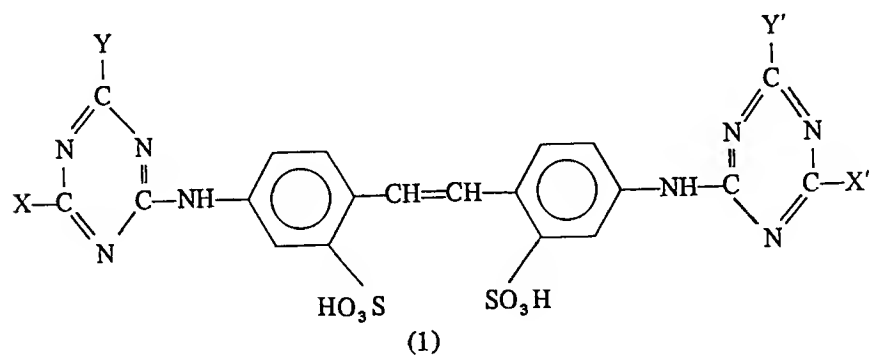
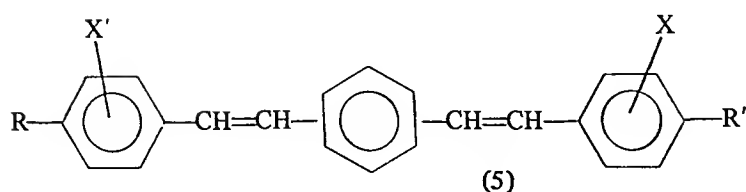


FIGURE 11-10
Reflectance curves of poly(vinyl chloride) alone (*O*), with violet dye (*V*), and with brightener (*W*) [19].

TABLE 11-4
Derivatives of (Di)aminostilbene(di)sulfonic Acid [18]



A = alkyl, aryl groups, etc.



R, R' = substituted amino, carboxyl, acetyl amino groups, etc.
X, X' = -H, -SO₃H

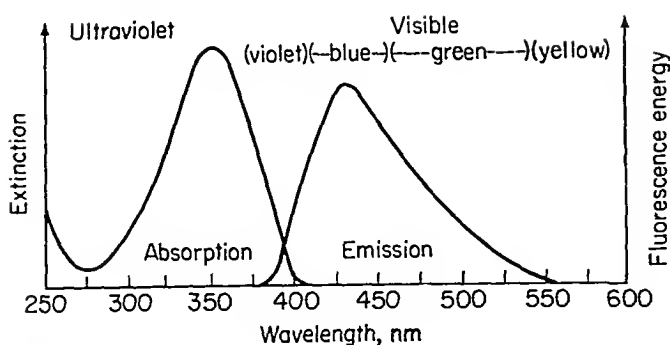


FIGURE 11-11

Absorption and emission spectra in solution for a compound of structure 1 in Table 11-4 [18].

to be added if a UV-absorber is incorporated in the same system to maintain a given intensity of whiteness.

As work with ionizing radiation (x-rays, gamma rays, electron beams) has increased, some means of protecting systems has been sought to interfere with degradation by radiation. In rubber, aromatic amines and phenolic compounds similar to the antioxidants and antiozonants already described are effective in decreasing the production of cross-links during gamma radiation [20, 21]. In aqueous poly(acrylic acid) solutions, Sakurada [22] reports that as little as 1 molecule of thiourea per 3 molecules of polymer will increase the dose of gamma radiation needed for gelation to occur by a factor of 5.

11-6 ABLATION

When a space vehicle reenters the earth's atmosphere (or any other planet's atmosphere), it adiabatically compresses the air in front of it. Aerodynamic heating also results from the viscous dissipation of energy in the layer of air around the vehicle. Using a reentering satellite as a frame of reference, the situation is the same as if air at a velocity $u = 6$ km/s encountering the nose of the satellite suddenly had its kinetic energy entirely converted to enthalpy (J/g of air). With an appropriate conversion of units, the result is a change in enthalpy of about 18 kJ/g air (8×10^3 Btu/lb). To interpret this in terms of a temperature is rather difficult. It can be appreciated that measures must be taken to protect the contents of a space vehicle from the heat. The actual heat load will vary with vehicle geometry, entry and flight path angles, velocity, and altitude. Some typical trajectories with their corresponding *stagnation enthalpies* are shown in Fig. 11-12. The heat load may be handled by heating up a large mass acting as a *heat sink*, by energy transfer by *radiation*, and by *transpiration*, where a coolant is pumped to the surface and evaporated much as the body is cooled by perspiration. In terms of cooling capacity and reliability a fourth method has been favored. *Ablation* can be defined as a sacrificial loss of material accompanied by transfer of energy. Polymers have been used in *ablative* systems for a combination of reasons. These have been summarized by Schmidt [23] as:

1. High heat absorption and dissipation per unit mass expended, which ranges from several hundred to several thousand Btu/lb of ablative material.

2. Excellent thermal insulation, which eliminates or reduces the need for an additional internal cooling system.
3. Useful performance in a wide variety of hyperthermal environments.
4. Automatic temperature control of surface by self-regulating ablative degradation.
5. Light weight.
6. Increase in efficiency with the severity of the thermal environment.
7. Tailored performance by varying the individual material components and construction.
8. Design simplicity and ease of fabrication.
9. Low cost and nonstrategic.

Limitations listed by the same author for polymers are:

1. The loss of surface material and attendant dimensional changes during ablation must be predicted and incorporated into the design.
2. Service life is greatly time-dependent. Present uses are for transitory periods of several minutes or less at very high temperatures and heating.
3. Thermal efficiency and insulative value are generally lowered by combined conditions of low incident flux and long-time heating.

The heat of ablation (the ability of the material to absorb and dissipate energy per unit mass) can be measured in various ways. In general it will be made up of the energy to heat the material up to a reaction temperature, the energy to decompose or depolymerize, the energy to vaporize, and the energy to heat the gases. Any exothermic reactions such as oxidation of hydrocarbons work in the opposite direction and lower the heat of ablation.

In addition to a high heat of ablation it is desirable that the material possess good strength even after charring. Any sloughing off of chunks of material represents poor usage, because the pieces have absorbed only enough heat to come to temperature and have not decomposed or vaporized. The various stages of heating, charring, and melting are profiled in Fig. 11-13 for two composites. It can be noted that the

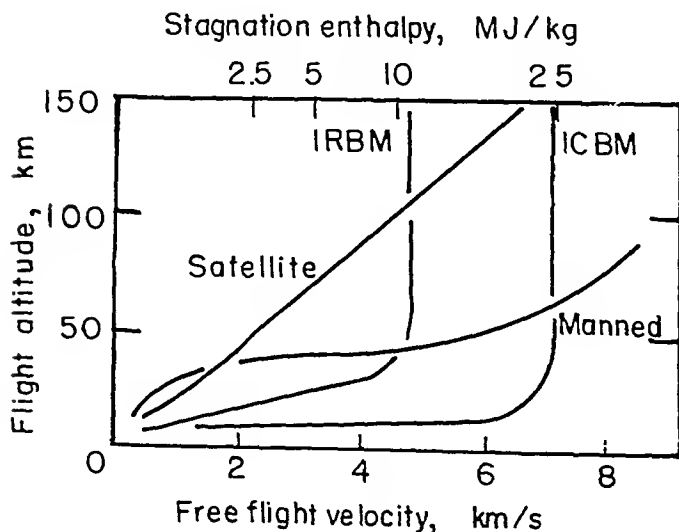


FIGURE 11-12

Representative reentry trajectories for various flight vehicles [23].

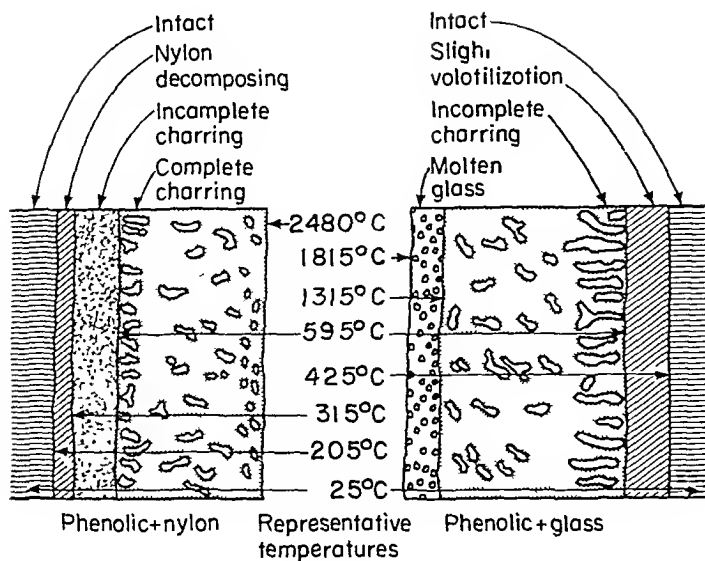


FIGURE 11-13

Temperature distribution in two plastics during steady-state ablation [23].

glass-reinforced system produces a molten glass surface, which can be an advantage mechanically. On the other hand, the nylon-reinforced system may have the higher thermal efficiency.

11-7 WASTE DISPOSAL AND RECYCLING

In recent years public attention has focused increasingly on the consequences of the population explosion coupled with an increasing worldwide standard of living. The two factors combine to produce various social problems. Perhaps the most obvious one is the energy crisis. However, waste disposal is another pressing problem. The bulk of typical municipal refuse is cellulose in the form of newspaper, packaging materials, cardboard, and the like (Table 11-5). Synthetic high polymers are present in the form of films and in molded plastics and rubber. These form a small but very persistent fraction of the whole. Within the overall scope of waste disposal, getting rid of polymeric materials, especially packaging material such as film and containers, has had a relatively low priority because it does not represent so much a health hazard as it does a kind of esthetic pollution, making our environment less pleasant to look at.

Another factor should be kept in mind. Urban waste is exceeded in magnitude by mineral and farm wastes by a large degree (Table 11-5). However, the disposal of urban wastes is concentrated in highly populated areas and represents a much greater health hazard to a large proportion of the population than does the disposal of mineral and agricultural wastes.

By far the most common method of refuse disposal is open dumping, although many large cities operate incinerators. Both of these methods are objectionable in that open dumping brings about rat infestation with consequent disease proliferation, and incineration aggravates the atmospheric pollution problem, already bad enough in most cities. The method most encouraged by various authorities is the sanitary land-fill

in which refuse is buried under a layer of soil. The covering discourages rats and odor development while the natural processes of biological decay can operate so that the land-fill area can be returned to agricultural or other uses eventually. Unfortunately, glass, metals, and synthetic polymers do not biodegrade appreciably. Very little waste is salvaged.

There are various alternatives available for dealing with the problem of waste disposal as it applies to packaging film and containers. The concept of reuseable containers has never been successfully employed except with glass bottles for soft drinks and milk. In addition to the obvious economic hurdles of collection and cleaning, one can also pose environmental objections to the use of the various cleaning compounds (often high in phosphates) that must be used. Recycling of materials has been attempted with glass bottles and aluminum cans. So far the costs of collection have discouraged the use of the method except where volunteer organizations have donated time or money. Among plastic bottles, polyethylene bottles can be ground up and molded into plastic pipe where clarity is not a requirement. The monomers of poly(ethylene terephthalate) used in beverage bottles can be recovered by hydrolysis or alcoholysis and subsequently can be used to make other polymers.

Incineration with energy recovery can be applied to most polymeric materials (along with cellulose and other components of refuse). A great deal of attention was received during the 1970s by polymers that break down on exposure to sunlight. The esthetic pollution by surface litter can be combatted by using materials that are inherently degraded by ultraviolet light or contain additives that sensitize degradation. Of course, materials buried in a landfill are not exposed to sunlight. There have been few actual commercial applications of the UV-degradable plastics despite their appeal. Soluble containers have been suggested from time to time. Both silica-based and organic polymeric materials can be used. Aside from the technical and economic difficulties of producing and using such "self-destructing" containers, their use does not solve the pollution problem unless the soluble products are biodegradable.

Some methods of utilizing polymeric refuse have been successful with specific

TABLE 11-5
Waste Disposal*

Composition of Typical East-Coast Municipal Refuse (%)		Waste Generated in United States per Year (kg $\times 10^{-9}$)	
Miscellaneous paper	25	Urban waste	360
Newspaper	14	Mineral wastes	1100
Garbage	12	Agricultural crop and animal wastes	2000
Glass, ceramics, and stone	10	Waste Disposal Methods (%)	
Grass and dirt	10		
Metals	8		
Wood	7	Open dumping	73
Cardboard	7	Incineration	15
Textiles	3	Sanitary landfill	8
Plastic film	2	Salvage	3
Leather, molded plastics, and rubber	2	Composting	1

*U.S. Public Health Service data for 1970.

products. Scrap tires are a case in point [24]. The simplest solution is to use the tires without modification as artificial reefs or as highway barriers. Other alternatives are shredding tires into scraps to be mixed with asphalt for highways, burning to recover fuel value, or pyrolysis with recovery of carbon black, gas oil, or fuel oil. For many years some rubber has been reclaimed from tires by chemical devulcanization. The first step is to reduce the tire to smaller dimensions. A *cracker* is a device consisting of two corrugated rollers turning at different speeds between which the tire is ground and torn into bits. After the metal bead is separated, the ground scrap is digested in a mixture of dilute alkali and organic solvents at an elevated temperature (150 to 200°C). The cycle can last anywhere from a few minutes to a few hours depending on the machinery involved. The major reaction is the breaking of polysulfide cross-links so that the network reverts to a branched, moldable material. The fiber reinforcement is either digested or removed in some other way. Reclaimed rubber retains most of the oils and fillers from the original tire so that it needs little additional compounding for many uses. The problem of identifying tires with various rubber components, the energy costs for reclaiming, and pollution control of reclaiming liquids have caused the production of reclaimed rubber to decline. In 1978 consumption of reclaimed rubber in the U.S. amounted to only 119×10^6 kg, compared to 346×10^6 kg in 1951. Total U.S. rubber consumption in 1978 was 3320×10^6 kg.

Thermoplastics are in principle much easier to recycle than cross-linked rubber. According to one source [25], the 13×10^9 kg of plastics produced in 1974 resulted in 6.5×10^9 kg of waste. The consumer waste consisted of film and other packaging material as well as discarded toys, household goods, appliances, and so on. Almost none of this was recycled. About 70% of the industrial waste was recovered (Table 11-6). Industrial waste includes off-specification material from polymer production and fabrication processes as well as material trimmed from extrusion and molding operations. Most sprues and flash from injection molding are recovered by simple regrounding and remolding. With some other thermoplastics, a reversion to monomer and repolymerization is worth the effort to get a clean, reliable product. It is not always economically sound for the fabricator to reclaim his own scrap. Dealers who collect materials from many sources are in a better position to combine materials and to supply more uniform product to molders.

TABLE 11-6
Waste Disposal in 1974 [25]

Type	kg $\times 10^{-9}$
Nonindustrial waste (not recovered)	3.8
Industrial waste	
Not recycled	0.8
Recycled in-plant	1.2
Recycled by reprocessors	0.7
Total	6.5

PROBLEMS

- 11-1. Why does a suspension of poly(vinyl chloride) powder in dioctyl phthalate on heating first become clear and then start to turn yellow?
- 11-2. In mechanical degradation of a polymer in solution, the rate of chain scission may be faster for higher-molecular-weight chains. If in Eq. (11-6) we have $k = k' x_n^a$, where a is a power greater than zero, derive an expression for x_n as a function of time.
- 11-3. Cite instances in which each of these "degradation" reactions is desirable: (a) hydrolysis, (b) cross-linking, and (c) depolymerization.
- 11-4. If a heat shield 5 ft in diameter is to be made from glass-reinforced polystyrene, how much heat can be removed by the depolymerization of a layer 1 in thick of polymer (70 vol percent polymer, 30 vol percent glass)? $\Delta H_{\text{vap}} = 153 \text{ Btu/lb}$ for monomer.

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12

FABRICATION PROCESSES

12-1 THE FABRICATOR

It is only in general terms that we can differentiate the fabricator from other participants who carry out the steps that change a fraction of natural gas into a sweater, a petroleum fraction into a garbage can, or linseed oil into a layer of paint. In every case, the first step is the production of a suitable monomer by a combination of physical separation processes such as distillation and extraction together with chemical reactions such as dehydrogenation and cyanoethylation. Polymerization of acrylonitrile and ethylene for two of the products mentioned is not considered to be *fabrication*, whereas the polymerization of linseed oil is. However, converting the polyacrylonitrile into a fiber, which may then be compounded, crimped, dyed, and twisted, does comprise fabrication. Likewise, taking the polyethylene pellets from the end of the polymerization process and injection-molding the can is a process of fabrication. For our purposes we shall consider the further processes of weaving or knitting cloth and the assembly of apparel as being beyond the scope of the fabricator. It can be seen from these examples that no unambiguous definition comes to hand. The fabricator sometimes starts with monomers or prepolymers, but more often with polymers. He changes the ingredients physically and perhaps chemically. His customer may be the ultimate user, as with the garbage can or paint, or his customer may be someone who changes the physical form again, as with the fiber for the apparel manufacturer. Several fabricators may add to the value of materials they process in sequence. One company may produce a rubbery polymer, a second may compound it, a third may convert it into a sheet, and a fourth finally may form the sheet into a gasket. Liaison between the polymer producer and the ultimate user is a difficult and demanding facet of polymer technology. Because the ultimate user often has limited technical resources and is preoccupied with immediate problems, most polymer and monomer producers have built up substantial *technical service* organizations to generate tech-

niques and materials (together with immense quantities of data) that guide fabricators and provide a basis for selecting the best polymers and fabrication conditions for a given application.

12-2 RAW MATERIAL FORMS

Liquid raw materials may be received in 55-gal drums or 8000-gal (30 m^3) tank cars. Smaller units such as carboys and cans may be used. Individual tank trucks and tank cars vary in capacity from one to another. Monomers and prepolymers often come as liquids. The large-scale producer of urethane foams receives polyols and diisocyanates in tank cars and uses them directly from the siding or perhaps transfers them to storage tanks. On a different scale, the familiar two-part epoxy adhesive can be bought as a pair of tubes in most hardware stores. Once again, the two liquids represent a liquid prepolymer and another reactive ingredient, in this case an amine hardener. Both epoxy systems and solutions of unsaturated polyesters in styrene monomer are used as liquids by fabricators of glass-reinforced structures, among which are auto bodies, boat hulls, and filament-wound rocket casings or storage tanks.

Most latexes are the result of emulsion polymerization processes. For the coatings industry no chemical change is necessary, and the compounder adds value to the product by mixing the latex with a stable dispersion of pigments, stabilizers, and other ingredients to make a protective or decorative coating. On the other hand the latex may be coagulated and cross-linked in the process of making a foam or dipped glove. It is important that the polymerization process leave no objectionable residues in the latex, because only very volatile ingredients can be removed economically. Not all latexes come from emulsion polymerization. Natural rubber latex is recovered from the tree. Polymers that are best produced by bulk or solution techniques can be converted into latexes by *post-emulsification*. In a typical process a polymer solution is emulsified in water with a surfactant, then the solvent is evaporated. Latexes of butyl rubber and polyethylene are available, even though neither is usually polymerized in emulsion.

It is rare that a polymer is supplied in the same solvent in which it was polymerized. For example, alkyd resins may be polymerized in the presence of toluene or xylene, but they are supplied to the paint compounder diluted with mineral spirits. A liquid dispersion of poly(vinyl chloride) in a plasticizer (Sec. 3-6) may be the raw material for a slush molder (Sec. 12-6).

Massive solid forms are common in the rubber industry. Bales of natural rubber may weigh 100 kg. Synthetic rubber is often sold in bales (blocks) that are wrapped in polyethylene or dusted with talc and weigh 20 to 50 kg. Polychloroprene is available in batons or smaller pieces that weigh less than a pound and are packaged in bags. For ease in dissolving rubber in solvents for coatings and adhesives applications, both natural and synthetic rubbers have been put in crumb form. The porous particles have a much greater surface area for solvent attack. Most thermoplastics for molding and extrusion applications are sold as pellets (often called "powder"), which are cylinders about 3 mm in diameter and length. In this form the polymer flows freely in automatic dispensing devices and in bins and hoppers. Thermoplastics are used as fine powders in rotational and fluid-bed coating systems (Secs. 12-4 and 12-6). Because the

fabricator may wish to compact a specific unit weight of a resin for compression-molding himself, most thermoset resins are supplied as powders that can be compressed at room temperature into cakes or "preforms." Poly(vinyl chloride) from suspension or emulsion polymerization is supplied as a powder. Suspension polymer particles range from 50 to a few hundred μm in diameter and are quite porous. They are dry-blended with plasticizers, yielding a dry, flowing, plasticized powder. The emulsion-polymerized resin is smaller in particle diameter and denser so as to be suitable for dispersion in plasticizers that are mobile liquids.

For many fabricators the raw form of the polymers they use is the result of a previous fabrication step. This is true of the sheet formers, since the molder of blister packages or refrigerator door liners seldom forms his own sheet but buys it from a separate converter. Builders of ductwork, storage tanks, and luggage commonly buy their raw materials as sheets, tubes, or other extruded shapes.

12-3 MIXING

Mixing low-viscosity liquids or blending dry powders can be accomplished with conventional equipment. Turbine and propeller agitators are used to mix low-viscosity liquids, and twin-cone blenders or tumblers are used for dry powders. These devices have low power requirements and rather low residence times. At the other extreme, the dispersion of a finely divided solid such as carbon black in a rubber with a viscosity of about a million poises presents a situation requiring more power.

The degree of mixing, the uniformity of dispersion of one phase in another, can be measured in several ways. One could take a series of samples of uniform size from a large batch and determine in each the concentrations of various ingredients. A statistical analysis coupled with a mathematical model can yield a number that can be fitted into a scale of uniformity or degree of mixedness. It is more common to judge the uniformity by some performance test. Mechanical failure tests such as tensile, tear, and impact strength are used. Optical tests are conventional for judging pigment dispersion. When an entire cable is tested for electrical strength through the insulation, a very sensitive measure of uniformity is obtained, since it takes only one pinpoint of poorly dispersed filler to bring about failure at a low impressed voltage.

For mixing liquids with viscosities less than about 10 P (1 Pa·s), paddles, turbines, and propellers are suitable. Power requirements vary from 0.5 to 15 hp/1000 gal (0.1 to 3 kW/m³). If a solid polymer is to be dissolved in a solvent, a mixing impeller with a saw-toothed edge is available that can cut the swollen solid ribbons in addition to circulating the contents of the tank (Fig. 12-1). On the other hand, the high speeds characteristic of some agitators can decrease the molecular weight of the polymer by a mechanical *shearing action*.

Mixing viscoelastic materials involves techniques different from those used with low-viscosity fluids. In the latter case, the normal procedure is to induce turbulence to a degree such that molecular diffusion can proceed rapidly to establish a uniform concentration of ingredients. With polymers it is necessary to use high local shear rates and rather gross mechanical "folding" to get the same result. A simple analogy to the two processes is the comparison between mixing cream in coffee and dispersing a spoonful of caraway seeds in a batch of bread dough. The power and time requirements are much more stringent for the dough, of course.

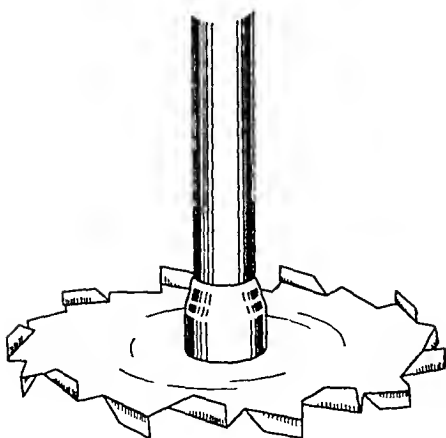


FIGURE 12-1
The impeller of the Cowles dissolver [1].

Pastes and liquids with viscosities higher than 100 P (10 Pa·s) are handled in machinery resembling that familiar in the baking industry. Kneaders and dough mixers are used to mix pigments in printing inks, to disperse poly(vinyl chloride) in plastisols, and to blend together the more viscous prepolymers and other ingredients for urethane foams. The agitator speeds are lower and the power requirements higher (10 to 1000 hp/1000 gal, or 2.5 to 250 kW/m³) than those for turbines and propellers.

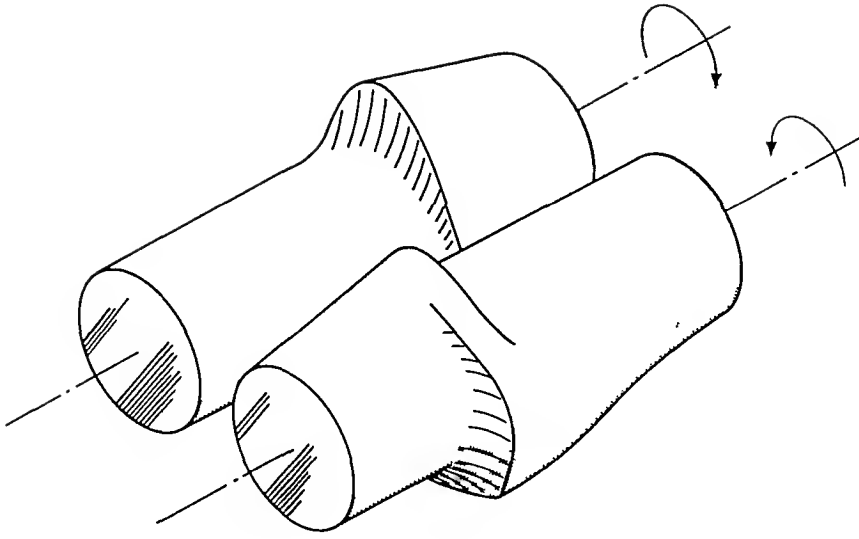
Amorphous polymers that are 50 to 200°C above T_g and have molecular weights in the range of 10^4 to 10^6 are most often mixed with solids or other polymers in intensive mixers or on mixing rolls. The intensive mixer is distinguishable from the dough mixers and kneaders by two features. One is the sturdier construction, which allows a higher power input per unit volume. The second is pressurized mixing, usually with temperature control. In the Banbury mixer two interrupted spirals (Fig. 12-2a) rotate in opposite directions at 30 to 40 rpm. Polymers, fillers, and other ingredients are charged through the feed hopper (Fig. 12-2b) and then held in the mixing chamber under the pressure of the hydraulic ram. Both the rotors and the walls of the mixing chamber can be cooled or heated by circulating fluid. In a typical application, a 600-hp (447-kW) motor might be used for a charge of 150 kg of rubber. This amounts to almost 3 W/g or about 0.7 cal/g·s. Even in a mixing cycle of a few minutes with cooling water, the temperature increase can be 30 to 60°C.

The mainstays of the rubber industry for over 50 years have been the two-roll mill and the Banbury mixer. Roll mills were first used for rubber mixing over 100 years ago! The plastics and adhesives industries adopted these tools later on.

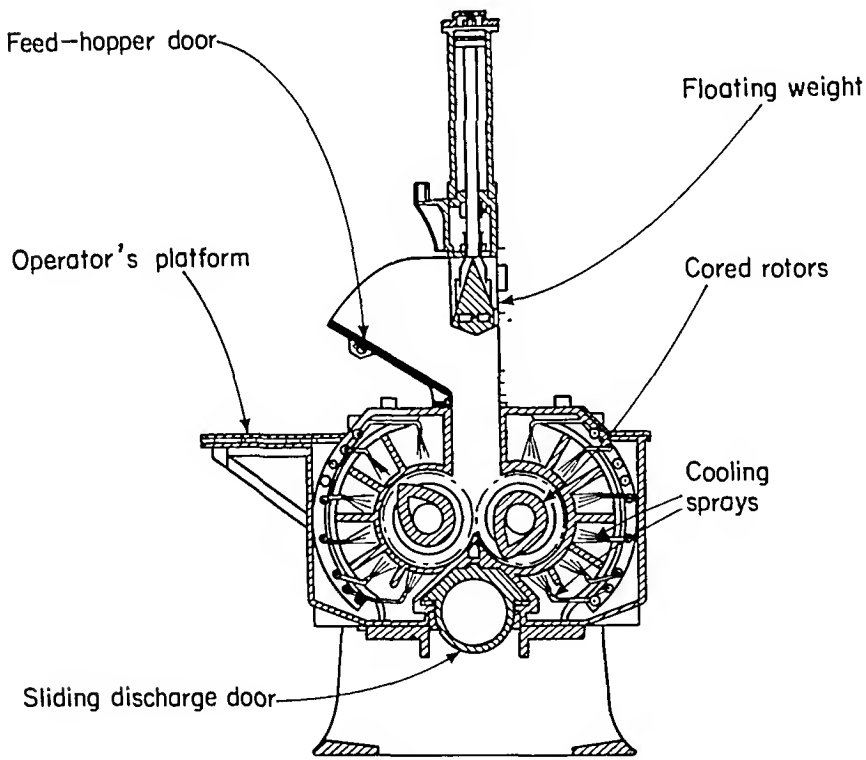
The two-roll mill shears the material in the nip between the rolls (Fig. 12-3), one of which is rotating faster than the other. Mixing is a function of:

1. Roll speeds
2. Amount of turnover (folding) between passes
3. Number of passes
4. Gap between rolls

The value of (1) is usually fixed in any machine; (2) and (3) are functions of the amount of material in a batch and time of milling. They are also functions of the viscoelastic properties of the material being mixed, since multiple passes often depend



(a)



(b)

FIGURE 12-2

(a) Roll mixing blades in the Banbury mixer. (b) Cross section of Banbury mixer. (Registered trademark of Farrel Co.) [2].

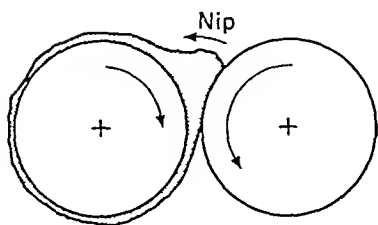


FIGURE 12-3
Two-roll mill.

on the material adhering to the roll and being carried around back to the nip. The value of (4) is usually changed fairly easily on most machines and is often decreased during the course of a single mixing operation.

In the Banbury mixer the material is subjected to less shearing than in roll mills, since the gap between scroll and wall is not adjustable. Also, heat transfer is more difficult, so that a temperature rise invariably is produced. However, incorporation of solids is more rapid because the mixing is done under the pressure of a hydraulic (or manual) ram. Also, the mixing depends much less on the viscoelastic properties of the material than does mixing on a roll mill.

Powders can be blended together by a simple tumbling action. In the ribbon blender, double-cone mixer, or twin-shell blender (Figs. 12-4 and 12-5) a simple rotational motion causes particles to be raised together and then to fall, splitting into small domains that are rejoined at random in the next cycle. Rolling and folding of the charge occur also. The same apparatus is used to blend porous poly(vinyl chloride) with plasticizers. Liquid plasticizer is poured or sprayed onto the powdered resin. During the tumbling, capillary action draws the liquid into the pores of the resin, so that in a few minutes the dry, powdery character is restored and the resin-plasticizer combination can be charged to some other equipment (extruder or calender) in which it will be fused into a continuous product.

Roll mills have been mentioned as functioning to mix polymers with fillers. The same equipment can be used not only to disperse a solid but to attrite it as well. Roll mills with up to five rolls, each rotating faster than the preceding one, are used to disperse pigments in paint master batches. A slowly rotating cylinder half-filled with ceramic balls is a familiar sight in the paint industry. The falling action of the balls (Fig. 12-6) decreases the size of solids and disperses them in a liquid at the same time. As opposed to the roll mills, which disperse the pigment in a few passes

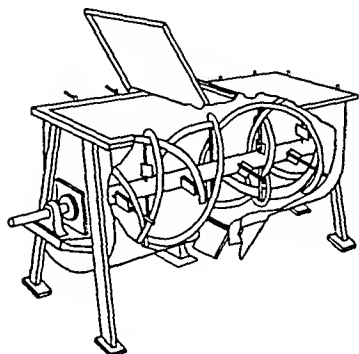


FIGURE 12-4
Ribbon blender [2].

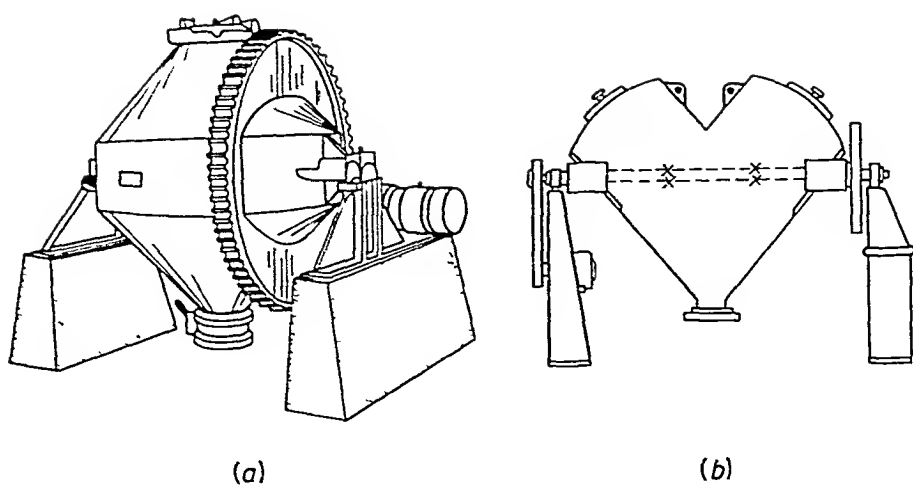


FIGURE 12-5

Tumbler mixers: (a) double-cone mixer, (b) twin-shell blender [2].

with an elapsed machine time of a minute or so, the ball mills usually operate on a cycle of hours or days.

It is obvious that less energy (and expense) is required to disperse solids in low-viscosity media than in rubbery polymer melts. In applications where a standard filler and plasticizer are being used in large amounts, the producer of a rubber may find it expedient to add the carbon black and oil to the latex before coagulating and baling it. About half the styrene-butadiene rubber supplied in recent years has had oil added

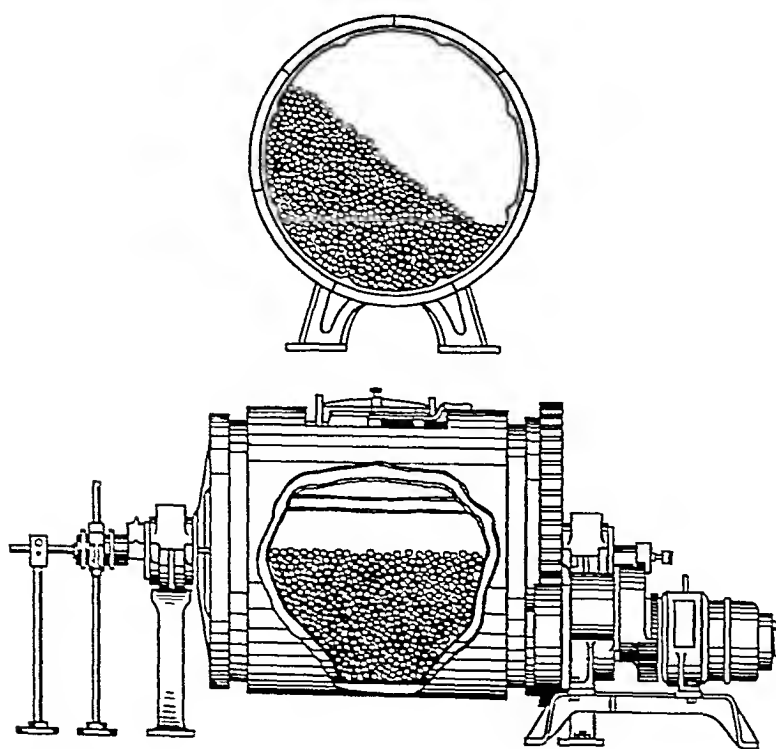


FIGURE 12-6

Cross-sectional and longitudinal views of a ball mill. (Patterson-Ludlow Division, Banner, Ind.) [2].

to it before coagulation (about a gram of oil for each 3 g of rubber in a typical formulation). Half of the oil-extended rubber has had carbon black added also (see Sec. 13-3). Master batching undoubtedly will continue to grow in popularity whenever a market justifies it to the polymer producer.

12-4 ONE-DIMENSIONAL PROCESSES

In the application of coatings and adhesives the only important dimension usually controlled is the thickness. There are many other parameters to be considered, of course. Adhesion is of overwhelming concern. In coatings, adhesion to one surface must be controlled. Adhesives often represent a more complicated situation because two unlike surfaces may be involved. On the other hand, the coating must face the challenge of its environment with its hazards of chemical, bacteriological, and mechanically abrasive attack over a high surface area. The adhesive seldom has to contend with these to the same extent.

Coatings

A coating is a thin layer of material intended to protect or decorate a substrate. Most often it is expected to remain bonded to the surface permanently, although there are strippable coatings that afford a temporary protection. We can subdivide coatings by considering whether or not they contain a volatile solvent or diluent and whether or not a chemical reaction is involved in film formation.

Nondiluent, Nonreactive

The oldest recorded use of polymers was for a coating of this type. The Lord told Noah, "Make yourself an ark of gopher wood; make rooms in the ark, and cover it inside and out with pitch" (Genesis 6:14). The pitch may have been a naturally occurring bitumen or wood rosin applied as a hot melt. A more recent application in which moisture impermeability is sought is the wax- or polyethylene-coated milk container now so familiar. The hot melt can be applied from a roll on a continuous basis. More commonly, the polyethylene might be extruded through a slot (Sec. 12-5, Extrusion) as a film layer and laminated with the cardboard. The formulation of a strippable hot-melt coating with ethyl cellulose as the binder is given in Table 12-1. The ingredients are melted together at about 190°C. Metal pieces such as drill bits or other tools and gears can be dipped in the molten mass and cooled in air with a

TABLE 12-1
Peelable Hot-Melt Coating [3]

Material	Parts by weight
Ethyl cellulose (50 cps grade)	25
Castor oil	10
Mineral oil	61
Paraffin wax	3
Stabilizer (antioxidant)	1

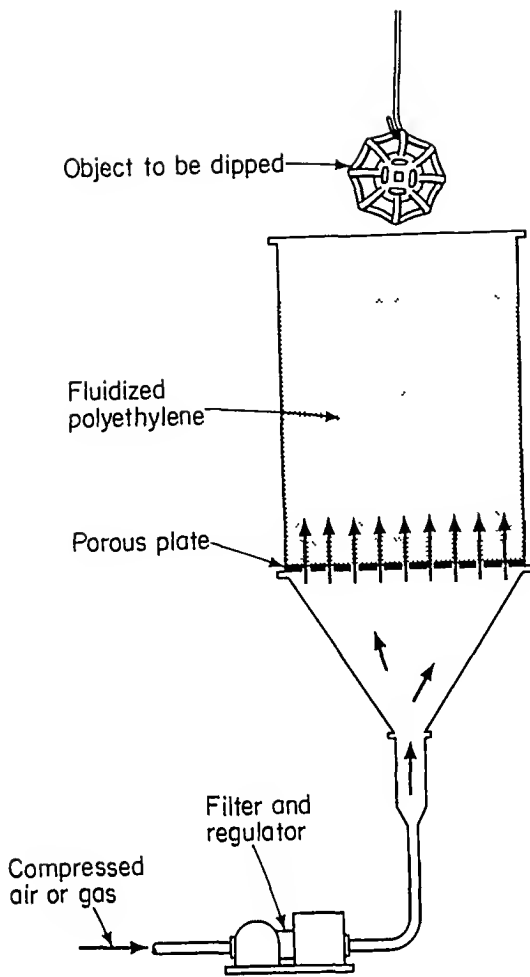


FIGURE 12-7
Fluidized-bed coating with powdered polyethylene [4].

thick (2 mm) coating. Castor oil is used as a plasticizer. Mineral oil and wax are less compatible than the castor oil, but they serve as lubricants as well as plasticizers. Exuding to the metal surface, they can function to prevent corrosion as well as mechanical abrasion during shipping and handling. The coating is easily stripped when the tool or other article is to be put into use.

Another application of nonreactive melt coating is *fluidized-bed* coating. In a typical setup (Fig. 12-7) a bed of powdered polyethylene in the range of 200 mesh (75 μm in diameter) is fluidized by the passage of air through a porous plate. A metal object to be coated is heated to well above the fusion point of the resin. When it is dipped into the bed and moved laterally as well, a layer of powder adheres to its surface and melts to form a continuous coating. The process is self-limiting because the metal cools as the polymer melts, and the layer of polymer is a poor conductor of heat. After being removed from the bed the object may be further heated to ensure the integrity of the film. There is nothing in the technique that limits it to thermoplastic coatings. The bed is not heated; only the surface of the object to be coated is hot. A mixture of powders that react when heated can be fluidized and a thermoset coating produced in the same equipment.

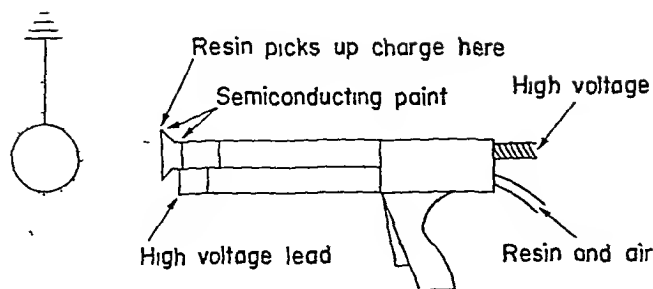
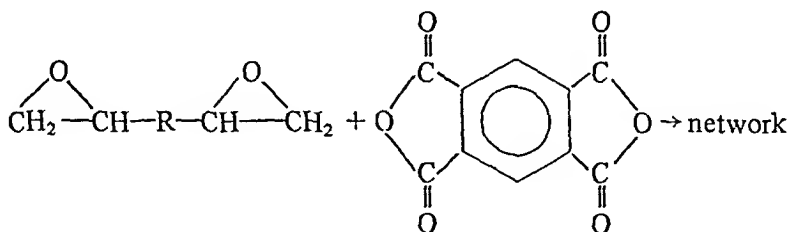


FIGURE 12-8
Electrostatic powder spray gun [5].

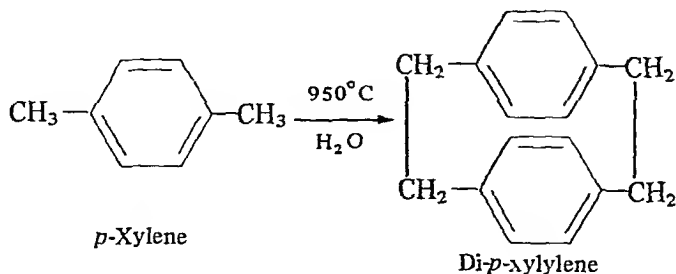
The powder can also be applied to a hot surface as a charged spray. Powder is carried by an air stream from a fluidized reservoir and through an orifice where it is charged by a high-voltage power supply (Fig. 12-8). The parts to be coated are grounded, so the charged powder is applied very efficiently to the desired locations. The part may be hot when it is coated or it can be heated subsequent to coating. Some applications of the electrostatic spray process are automobiles, appliances, metal furniture, luggage hardware, and even glass bottles [6].

Nondiluent, Reactive

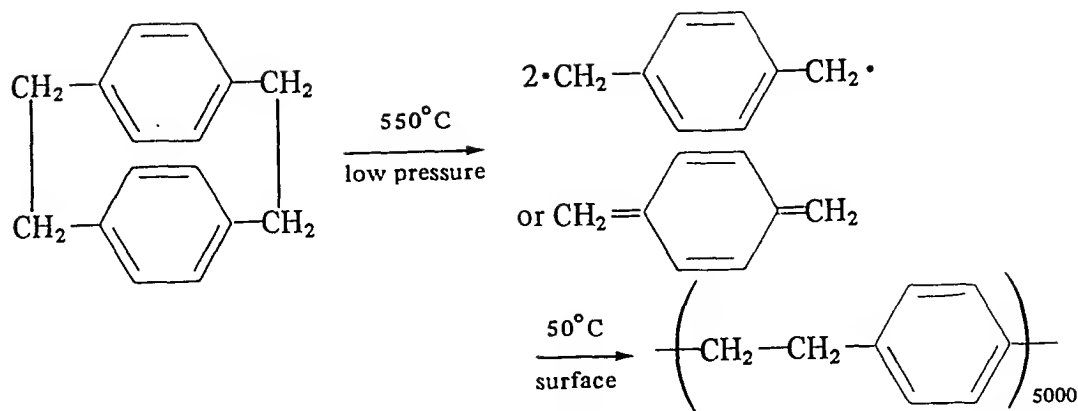
The fluidized-bed method can be used when the polymer is a reactive powder. A mixture of an epoxy resin and an acid "hardener" can be fluidized and deposited simultaneously. Reaction occurs only on the hot surface.



A general technique has been developed whereby a reactive monomer is sprayed on a surface and forms a polymer immediately. In one application the monomer is di-*p*-xylylene formed by the pyrolysis of *p*-xylene at 950°C in the presence of steam [7]:



When the purified monomer is heated to about 550°C at a reduced pressure, a diradical results in the vapor phase, which when deposited on a surface below 50°C polymerizes instantaneously to a molecular weight of about 500,000:



The thin, adherent coating can be applied to metals or to other substrates. A major application has been production of miniature capacitors having the polymer as a dielectric.

The process of producing polymers on a surface through the use of ionized, gaseous plasmas has been used with hydrocarbons, fluorocarbons, and other systems [8]. In glow-discharge polymerization, the surface to be coated can be made the anode for an electrical discharge over a potential of several thousand volts. Monomers adsorbed on the surface can form highly adherent, and often cross-linked, films. Another technique that makes use of plasma technology uses polymer powders rather than monomers. The plasma in this case consists of an inert gas such as argon passed through an electric arc so that its temperature is raised to 5000 to 8000°C. Poly(tetrafluoroethylene) powder is blown at high velocity through the plasma jet and onto the surface to be coated. As the polymer impinges on the surface it is sintered to a continuous coating.

In a special class of nondiluent, reactive systems are those that react because of high-energy radiation. Coatings that are useful are usually based on unsaturated molecules. They may contain reactive, nonvolatile monomers as well as a photoinitiator. It has been pointed out that Egyptian mummy wrappings were made from linen saturated with oil of lavender and bitumen of Judea and then exposed to sunlight [9]. The nontacky composite that results is quite durable, as visitors to the British Museum can attest. As a modern-day example, a photocurable printing ink might include an acrylated urethane polymer (containing pendant unsaturation), several monomers such as neopentyl glycol diacrylate and *N*-vinyl pyrrolidone, a sensitizer such as a benzoin ether or benzoquinone, and various pigments. The ink is transferred to a surface by conventional printing press processes. When such an ink is applied to a metal surface under an inert atmosphere, conversion to a dry, smudge-proof film can take place in seconds under a strong UV lamp rather than by evaporation of a solvent or by oxidation of a drying oil, which would take much longer. The monomers act as diluents in the system, but they react to become part of the film and are not evaporated.

Photoresists have been used for many years in lithography for the production of printing plates. Strictly speaking, these generally are applied from a solution. However, since the reaction takes place well after the film has been dried, they are included here in the nondiluent category. Chromated gelatin is one classical example that still finds some use in making masks for silkscreens. Somewhat newer are films made from poly(vinyl alcohol) containing bichromate. For a printing process the film might be

deposited on a metal surface from an aqueous solution. The dry film on exposure to UV light through a mask is insolubilized by oxidative cross-linking. Patient washing with warm water removes the unexposed portions of the film. Next the film is baked to increase adherence of the cross-linked portions. Then an etchant is applied to attack the metal and to leave a raised pattern where the polymer was irradiated. The polymer "resists" the etching of the metal. In some applications etching is not needed, as when ink receptivity is different for bare metal compared to a polymer surface. Another application of the poly(vinyl alcohol)-bichromate system is in the production of color television tubes. The screen of the tube requires a pattern of three types of phosphor dots. Each of the three phosphors can be applied in separate stages by exposure through a carefully registered set of masks. In each of three stages a single phosphor is suspended in the polymer film and the dots are insolubilized. The un-cross-linked polymer with its phosphor content is washed away. Etching is not required. The screen is baked between stages to oxidize the polymer film and to leave the phosphor firmly attached to the glass. The glass screen is fused on to the front of the TV tube with the phosphors on the inside surface.

The production of semiconductor devices, especially integrated circuits, represents the most demanding set of conditions for polymeric resists. Many silicon "chips" used in calculators and computers are produced in some variation of the following sequence of operations:

1. A silicon wafer about 76 mm diameter has one surface oxidized to a controlled depth.
2. Polymer is applied by placing a few drops of solution at the center of the oxide side of the wafer and then spinning the wafer to obtain a thin, uniform coating that when dry is several micrometers thick. A typical polymer would be poly(vinyl cinnamate) (see Sec. 13-5) or cyclized rubber (see Sec. 11-3).
3. Exposure to UV light through a mask insolubilizes part of the polymer.
4. Un-cross-linked polymer is washed off. Organic solvents are more common than water for applying and removing semiconductor photoresists.
5. The bare substrate parts are etched through the oxide layer down to the silicon layer by a fluoride solution in water or by a plasma containing reactive ions.
6. The chemical composition of the etched regions are altered. Ion implantation can be used to introduce "dopants," that is, impurities that make semiconductors of the diffused-base transistor type. Other operations can include depositing a layer of aluminum to act as a conductor or other materials to act as insulators.
7. All polymer is removed by solvents, plasmas, or baking.
8. The wafer is recoated and a new pattern imposed and processed. This entire sequence may be repeated a number of times to give integrated circuits with many layers and amazing complexity. The minimum line widths on chips produced by photolithography usually are in the 5- μm range. Experimentally, line widths of less than 0.1 μm have been achieved. The wafer is processed as a unit, but it may be cut up to produce hundreds of individual chips each only 5 $\times$ 5 mm in size. Attaching electrical leads to the tiny conducting spots on the chip is a separate, demanding task.

When the polymer is insolubilized by radiation, as in this example, the material is called a *negative* resist. It is possible to make polymers that become soluble on irradiation to give *positive* resists. One such positive resist is a polymer with pendant naphthoquinone diazide groups. The Wolff rearrangement converts the hydrophobic diazoketone to a hydrophilic carboxylate unit that is soluble in dilute alkali (Fig. 12-9).

To produce large-scale integrated circuit (LSI) devices, minimum line widths must be decreased to pack more circuits on a chip. Electron-beam lithography is used to produce masks for UV-photolithography and, in some places, to produce the chips themselves. A scanning electron beam similar to a scanning electron microscope can be programmed to produce patterns on a very thin polymer layer (less than $1\text{ }\mu\text{m}$ thick). The electron beam may cause cross-linking or may solubilize the polymer. Both poly(methyl methacrylate) and poly(butene-1-sulfone) respond to electrons by chain scission. The lower molecular weight polymer produced is more soluble than the original. Another type of radiation that has been used for lithography is high-energy x-rays. A major problem has been the long times of exposure needed compared to the UV and electron-beam.

Diluent, Nonreactive

The term *lacquer* usually connotes a solution of a polymer. Once used for solutions of naturally occurring polymers like shellac in alcohol, the term now is applied to all solutions in which film formation results from mere evaporation of the solvent and does not require that a chemical reaction take place. Another name sometimes used as a synonym for lacquer is *dope*. Airplane dope, for example, is a lacquer applied to fabric that has been stretched over airframes and other surfaces to increase tautness and decrease permeability. Film formation from a lacquer requires only the evaporation of solvents. Mixtures of solvents are usually needed in order to achieve a smooth, coherent film. Compatibility, often guided by the solubility parameter concept (Sec. 2-4), obviously is important. Volatility is adjustable by using solvents of different molecular weights or by using mixtures of solvents and *diluents* (extenders that may not be good solvents when used alone). As the coating dries, dimensions change, and

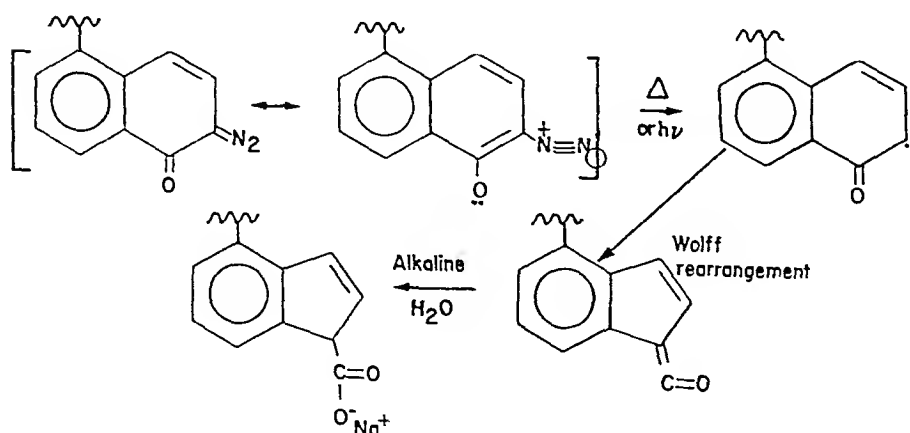
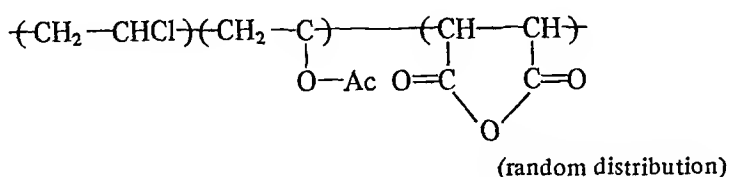


FIGURE 12-9

Photochemistry of diazoketone attached to a polymer chain, including subsequent Wolff rearrangement to carboxyl.

the change is more rapid at the surface. A proper balance of volatility and compatibility assures that the film will not “skin over” on its surface and create a barrier to further diffusion of solvent from the film. If a good solvent is too volatile, a poor one left behind in the film may reach a concentration where the polymer precipitates, giving a dull or wrinkled film. When the humidity is high, the surface may cool from evaporation of solvent and condense water. The water in turn may cause precipitation of the polymer, giving the film an undesirable opacity (*blushing*). A typical lacquer formulation (Table 12-2) contains polymer, pigment, plasticizer (nonvolatile solvent), and volatile solvents. The vinyl resins used here are copolymers of vinyl chloride with about 10 to 20% vinyl acetate. The VMCH also contains a few percent of maleic anhydride as a termonomer. This lacquer is designed for steel surfaces, and the acid functionality results in good adhesion to the iron surface.



Vinyl chloride, vinyl acetate, maleic anhydride terpolymer (VMCH)

It should be noted that we have classified this as a lacquer because reaction is not essential to film formation even though a reaction between the anhydride and the metal surface is possible. Titanium dioxide is widely used as a white pigment because of its excellent *hiding power* (ability to mask the substrate per unit weight of pigment). The tricresyl phosphate is used as the plasticizer in sufficient volume to lower the glass-transition temperature to about 40°C. Thermoplastic (un-cross-linked) binders for coatings usually are formulated to have T_g somewhat above room temperature. Too high a T_g gives a brittle film that may flake off when the temperature is cycled because the coefficient of expansion for metals is so much smaller than that for polymers (Sec. 10-5). Too low a T_g gives a soft film that will not resist abrasion. Vinyl chloride polymers, cellulose derivatives (acetate and nitrate), and acrylic copolymers can be formulated to remain tough over a wider range of temperatures than most homopolymers, so they have been favored for lacquers.

TABLE 12-2
White Vinyl Topcoat [10]

Material	Pounds
Titanium dioxide	100.0
Vinyl resin (VAGH)	66.7
Vinyl resin (VMCH)	66.7
Tricresyl phosphate	25.0
Methyl isobutyl ketone	288.0
Toluene	288.0
Total	834.4
Weight per gallon	8.34 lb

TABLE 12-3
White Latex Paint for Exterior Application [11]

Material	Parts by weight
Vinyl-acrylic polymer latex (Ucar Latex 180) (55% solids)	400
Pigments: Rutile TiO_2 175	375
Anatase TiO_2 50	
Mica, water-ground 25	
Talc 125	
Wetting agents, dispersants, surfactants	14
Phenyl mercuric acetate (30% solids)	5
Defoamer	5
Carbitol (diethylene glycol monoethyl ether)	15
2-Ethylhexyl acetate	5
Ethylene glycol	20
Water (added to latex during formulation)	293
Total	1132
PVC = 36%; lb/gal = 11.3	

Some homely examples of lacquers include the spray cans of "touch-up paint" sold to the auto owner. Most of these are pigmented acrylic resins in solvents together with a very volatile solvent that acts as a propellant (usually a low-molecular weight hydrocarbon). Model airplane dope may be a solution of cellulose acetate-butyrate in a mixture of ketones and aromatic solvents.

The latex paints are another class of coatings that form films by loss of a liquid and deposition of a polymer layer. During World War II the latexes resulting from emulsion polymerization of styrene and butadiene for rubber were found to be well-suited to film formation. The fast drying, low odor, and, above all, the ease of cleaning up spots and applicators when water is the diluent contributed to a do-it-yourself movement of tremendous proportions. A parallel rise in the wage level of painters and other craftsmen accelerated the process. The formulation of a modern latex paint is not a matter of merely dispersing a pigment in a latex, however. Some ingredients listed in Table 12-3 for an exterior, light-toned paint based on an acrylic-vinyl copolymer (Ucar Latex 180) include pigments (TiO_2 , mica, and talc), surfactants for dispersing the pigment in addition to the surfactant remaining in the latex from polymerization, a mercuric salt as a mildew preventative, a defoamer (needed during mixing and during application to decrease trapped air bubbles), and plasticizers. The ethylene glycol also functions as an antifreeze, since freezing and thawing can break a suspension and bring about coagulation. The term PVC in Table 12-3 refers to the *pigment volume concentration*, which is the volume percent of pigment in the non-volatile portion of the formulation (film ingredients). The pounds per gallon is important to the formulator, since he will ordinarily buy his ingredients by the pound, but he will sell his paint by the gallon.

As in the case of lacquers, the T_g of a latex paint polymer usually is adjusted by copolymerization or plasticization to the range of 30 to 50°C. Film formation proceeds differently, however. One can picture the latex particles as so many marbles

being deposited on a surface. As the water evaporates or, on wood and plaster surfaces, diffuses into the substrate, the spherical particles approach each other more and more closely. The minimum temperature at which the particles will coalesce to form a continuous layer depends mainly on the T_g . The water may have some plasticizing action, so the actual T_g may be slightly lower than one that might be measured in dry test. The driving force tending to push the particles together is related to the capillary pressure of water in the system. Smaller particles and higher surface tensions should result in lower film-forming temperatures. In practice it is found that the ratio of monomers or addition of plasticizers is a better control for film formation than particle size or surface tension [12].

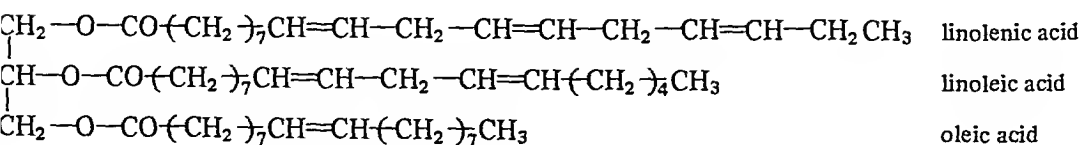
While most latex house paints fall in the nonreactive class, many applications use a subsequent cross-linking reaction to enhance durability. In a simple example, pendant hydroxyl and carboxyl groups on a polymer chain may not react with each other while the polymer is suspended as a latex. But when the film is dried and heated, esterification can take place. It may be possible to wash off a fresh film with soap and water, but not one that has aged and become cross-linked. The advantages in an exterior house paint are obvious because cleaning up is easy but permanence (water-resistance) increases with time.

Another broad application of latex films involving very low pigment volumes is the whole field of water-based polishes for industrial and home use. A typical material for vinyl tile floors consists of a polystyrene or acrylic copolymer latex of fine particle size together with plasticizers, waxes, and hard resins totaling almost the same weight as the polymer. The total solids content in the final product might be only 10 to 20%.

Latexes have also been used as paper coatings, as wet-strength promoters in paper, asphalt dispersions, and in concrete. In each case it is the binding action of the continuous film formed when the water is gone that is sought.

Diluent, Reactive

Although the term "paint" is used for latex-based as well as many other systems, some favor its use to describe one of the oldest coating systems known, that of a pigment combined with a drying oil and a solvent. The brown house paint of Table 12-4 does not differ in principle from coatings used hundreds of years ago. Linseed oil is a *drying oil* by virtue of its multiple unsaturation. In effect, the oil is a polyfunctional monomer that can polymerize ("dry") by a combination of oxidation and free-radical propagation. Modern methods of recovery by pressing and extraction remove almost all of the oil content (about 40%) of the flaxseeds. The oil is a triglyceride of a mixture of fatty acids. About half the fatty acid content is linolenic acid, another 20% is linoleic, and another 20% is oleic:



Typical triglyceride from linseed oil

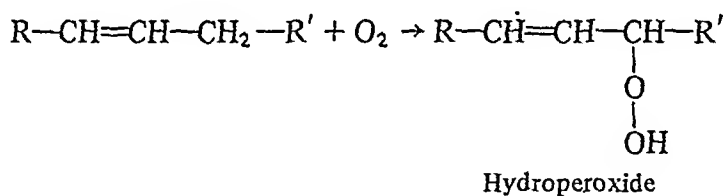
One can distinguish three stages in the film formation of a drying oil by oxidation. In the first, *autoxidation*, the oil reacts with oxygen to form peroxy compounds.

TABLE 12-4
Brown House Paint [13]

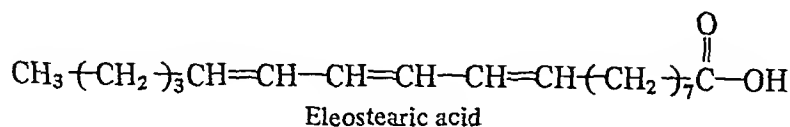
Material	Pounds
Iron oxide brown	64.0
Acicular ZnO	254.0
Calcium carbonate	600.0
Soya lecithin	4.6
Raw linseed oil	280.0
Kettle-bodied linseed oil (X viscosity)	93.0
24% lead naphthenate	9.3
6% manganese naphthenate	1.1
Mineral spirits	108.9
Total	1414.9
Pigment volume	35.8%
Consistency	83 KU
Weight per gallon	14.1 lb
Add puffing agent to increase viscosity	

In the second, *network formation*, the peroxy compounds react to create covalent bonds between the original drying oil molecules. In the third, much slower, stage, *aging*, the polymer film continues to react with oxygen, forming additional cross-links and also some volatile products.

In oils with isolated double bonds, autoxidation proceeds by the formation of hydroperoxides adjacent to the unsaturation:



Oils with conjugated unsaturation, such as tung oil with about 80% eleostearic acid, react more rapidly with oxygen, forming cyclic peroxides together with other oxygenated species.



Oil-soluble metallic soaps are used to catalyze the oxidation process. The time necessary to change a film of linseed oil to an insoluble network is decreased from days to hours by the addition of 0.05% cobalt metal in soluble form. Cobalt, manganese, and lead are commonly used as salts (soaps or *driers*) of naphthenic acid. The acid, a by-product of naphthenic lubricating oil refining, is predominantly composed of saturated, cyclic, monocarboxylic species. With a typical molecular weight of 150 to 250,

the acid yields soaps with excellent solubility in aliphatic solvents and good drying activity. The metallic soaps accelerate the rate of oxygen uptake and network formation and may also alter the details of the mechanism. In Fig. 12-10 linseed oil by itself increases in acid content much more slowly than it does with added metallic driers. The gain in weight shown is the net gain. It has been demonstrated that linseed oil may react with oxygen to the extent of 48% of its original weight over a period of several months. The net gain may be only 15 to 20% because volatile products, mainly CO_2 , are lost.

The pigments in Table 12-4 include calcium carbonate and zinc oxide, which would give a white appearance of moderate hiding power. The iron oxide gives a durable brown color, which is stable over a long period of time. The soya lecithin is a substituted phosphoric acid ester of a diglyceride that acts as a dispersing and stabilizing agent for the pigments. Kettle-bodied linseed oil has been heated with enough oxygen to cause some cross-linking, which increases the molecular weight and viscosity.

In the slow process of aging or weathering, the gradual erosion of the surface that accompanies further oxidation is not always undesirable. A *chalking* paint, one that erodes at the surface, is self-cleaning. In a house paint this means that atmospheric dirt will be removed from the surface along with some of the film by ordinary wind and rain or by deliberate washing.

Oleoresinous *varnishes*, as the name implies, are combinations of resins and drying oils. Prior to the introduction of alkyd resins in the 1920s (discussed next below), the term "varnish" usually denoted the reaction product of a heat-treated natural resin with drying oil. The product often was dissolved in a solvent, called a *thinner* because it decreased the viscosity of the varnish, together with appropriate driers. Addition of a pigment to a varnish yields an *enamel*, although the terminology

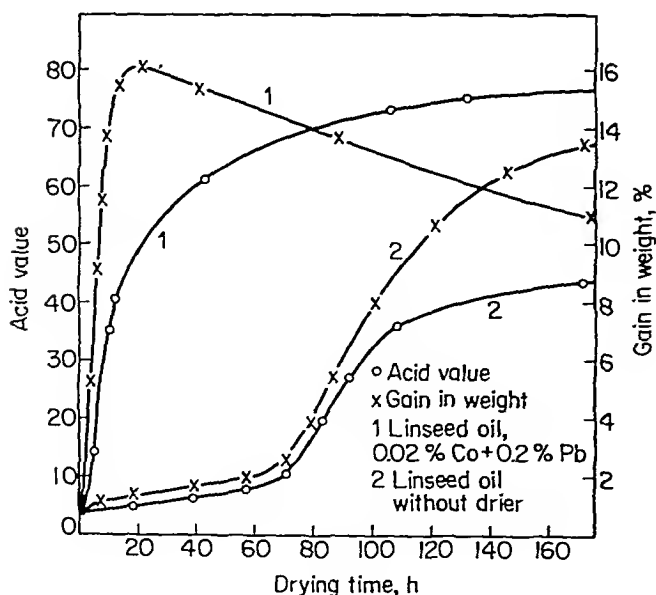
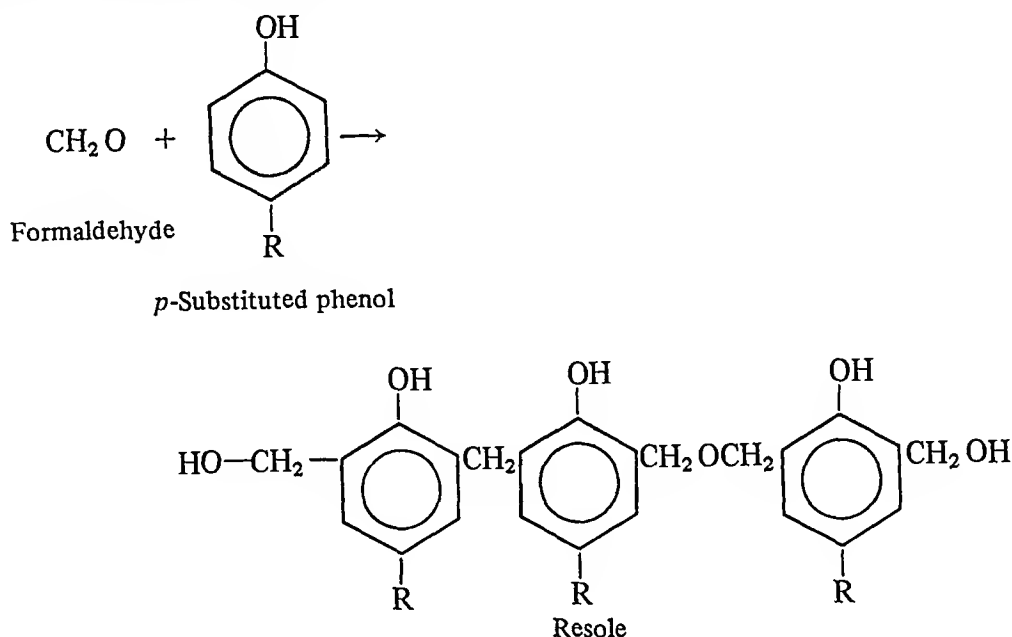


FIGURE 12-10

Acid value and gain in weight of linseed oil film on drying [14].

is far from standardized. The natural resins are not widely used any longer. The synthetic resins that are used often are somewhat complex. A simple example is a phenolic *resole*, a reactive, soluble material. Reaction of formaldehyde with a para-substituted phenol under alkaline conditions yields the resin, which can be further reacted with an oil to form an air-drying coating.

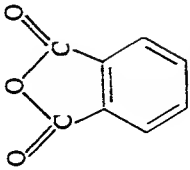


The reaction at 200 to 250°C with a triglyceride such as tung oil is accompanied by the evolution of water, so presumably the resole reacts with free acid groups from oxidation of tung oil as well as by ester interchange with the terminal hydroxyls of the resole. Other reactions involving the phenolic hydroxyl are probable also. The combination of hard, wear-resistant resin with softer, energy-absorbing drying oil films can be designed to give products with a wide range of gloss and durability. The terms long oil and short oil are used to denote varnishes that are higher and lower in the ratio of drying oil to resin, respectively.

Another route to balancing drying properties, durability, gloss, and hardness is the alkyd resin. These esters are formed from *alcohols* and *acids*, hence the coined name "alkyd." Originally the procedure resembled the cooking of an oleoresinous varnish in that a drying oil would be transesterified with a mixture of polyfunctional acids and alcohols. A common mode of operation today is to start with the free fatty acids from the drying oil rather than with the triglycerides. Another source of unsaturated fatty acids is the sulfate pulping process for making cellulose from pine chips. When the chips are digested at 170°C with sodium hydroxide and sulfide, a dark, odoriferous, pasty mass is extracted, which when evaporated and neutralized is crude tall oil, a mixture of rosin and fatty acids. Distillation separates the acids into fractions one of which is high in unsaturation. A typical analysis might show equal amounts of oleic and linoleic acids. The formulations of three typical alkyd resins based on tall oil fatty acids are indicated in Table 12-5.

The layout of a typical alkyd resin plant is shown in Fig. 12-11. The heart of the process is a jacketed 200- to 4000-gal kettle, usually of stainless steel. For temperatures of 200 to 300°C the circulating fluid in the jacket may be Dowtherm, a

TABLE 12-5
Typical Alkyd Resin Formulations*

Ingredient	Formula	Molecular weight	Long oil, parts by wt	Medium oil, parts by wt	Short oil, parts by wt
Tall oil fatty acids	—	ca. 280	123.2	49.1	39.6
Phthalic anhydride		148	50.0	28.2	58.7
Pentaerythritol	$C(CH_2OH)_4$	136	40.5	18.6	51.7
Trimethylol propane	$CH_2CH_2C(CH_2OH)_2CH_2OH$	134	—	—	—
Ethylene glycol	$HO-CH_2CH_2-OH$	62	—	4.1	—
Final concentration in mineral spirits, % solids			70	50	60
Total cooking time, h			6.5	7	5.5
Cooking schedule			Charge all ingredients. Raise temp to 250°C. Hold with inert gas and removal of water for acid number less than 6.	Charge all plus 6.5 parts xylene. Heat to reflux temp 230°C, and hold for acid number less than 8.	Charge as with long oil. Hold at 230°C for acid number less than 10.
Application			Trim and trellis paints. Air-dry in $\frac{1}{2}$ h with driers.	Industrial enamels. Air-dry in 40 min with driers and TiO_2 pigment.	Appliance enamel. Bake 20 min at 300°F (no driers).

*Gilliden-Durkee Div. of SCM Corp.

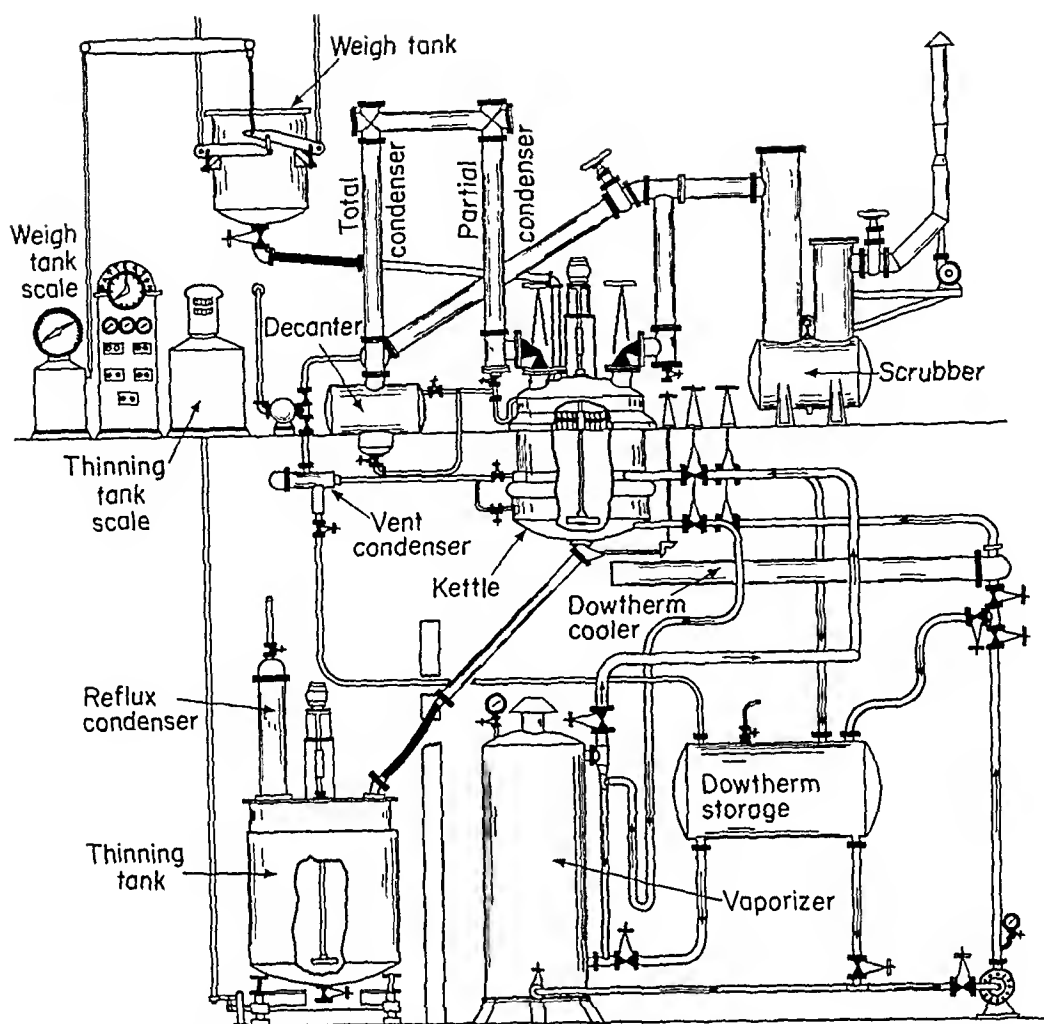


FIGURE 12-11

Processing system for alkyd resins heated and cooled by Dowtherm. (Patterson-Ludlow Division, Banner, Ind.) [15].

proprietary mixture of diphenyl and diphenyl oxide. To protect the drying oils from oxygen and to remove water, an inert gas such as carbon dioxide or nitrogen is sparged through the kettle. In the medium-oil example of Table 12-5 xylene is added, and since it is the only volatile ingredient, it refluxes and controls the temperature. When the vaporized xylene is condensed in a side arm, water that condenses with it can be removed in the decanter and only the xylene is returned to the kettle. This "azeotropic" process is somewhat faster and gives more uniform product than straight fusion. However, one has to contend with slightly more complicated equipment together with the fire hazard of the volatile solvent.

The *acid number* is defined as the weight of KOH in milligrams needed to neutralize 1 g of sample to a phenolphthalein end point, usually in a water-methanol mixed solvent. Because an excess of hydroxyl over carboxyl is used, the acid number is a good indication of the approach to complete reaction.

The finished resin is very viscous and flows with difficulty from the kettle even at the elevated temperature. As indicated in Fig. 12-11, the batch is dropped to a

thinning tank, where it is diluted with a volatile solvent, often mineral spirits, a petroleum cut. Even in solution, the final product has a viscosity of 10 to 100 P (1 to 10 Pa·s). Although the large paint producers make most of their own resins, there is a substantial market in resins that are sold to paint formulators who, in turn, serve the industrial and household consumers.

The drying mechanism for alkyd resins should resemble that described for linseed oil. It should be noted that some applications (short oil, Table 12-5) do not use driers but react in a short time at an elevated temperature.

A major influence on the coatings industry is the legislation enacted over the past several decades limiting the discharge of solvents into the atmosphere [16]. It is seldom economical to recover or incinerate solvents even in concentrated industrial applications. The smog problem in Los Angeles County, California, led to the adoption of "Rule 66" in 1966. This rule, which limits the discharge of "photochemically reactive solvents," was widely copied in other locales so that the term "Rule 66" has acquired international acceptance despite local variations. Besides defining certain solvents and combinations of solvents as photoreactive, the rule also limits total emissions of nonreactive solvents. The basic premise is that some aromatic compounds, branched-chain ketones, and unsaturated compounds react with nitrogen oxides in UV light giving rise to smog. Smog, in turn, is manifested by poor visibility, eye irritation, and plant damage. Although the particular conditions of Los Angeles are not found in many other places, Rule 66 has been adopted in some form in many locations, especially urban areas where automobile exhaust raises the nitrogen oxide levels. The obvious answer to Rule 66 was, at first, reformulation with the allowed solvents. However, with the limitation on solvent vapor discharges of all kinds, there has been a trend toward water-borne coatings, powder coatings, and UV-curable (100% reactive) coatings.

Adhesives

In the broad sense of the word, adhesion is important in every heterophase system including the coatings just described. However, we can look at the process more narrowly as involving a layer of material (the *adhesive*) between two surfaces (*adherends* or *substrates*). *Mechanical* adhesion is easy to visualize. When two porous surfaces such as paper are glued together with a liquid adhesive, the interlocking action of the liquid that penetrates the pores acts as a mechanical fastener. On the other hand, gluing together two smooth, impervious surfaces must involve other forces. In *specific* adhesion the secondary forces between adhesive and surface bond the two. Actual covalent bonds may be formed, but this is hard to demonstrate in most cases. In any kind of adhesion, wetting of the surface by the adhesive is important. One way of characterizing a surface is to measure the *contact angle* θ_c made by a drop of liquid on the surface at the point where the two phases meet (Fig. 12-12). Perfect wetting occurs when $\cos \theta_c = 1$, that is, when $\theta_c = 0$. When $\cos \theta_c$ is plotted for a series of liquids on a single surface, the intercept at $\cos \theta_c = 1$ is γ_c , the critical surface tension of that surface (Fig. 12-13). The values obtained for some common polymers are summarized in Table 12-6. In general, liquids will spread when the surface tension of the liquid is lower than the critical surface tension of the surface. Thus glass and

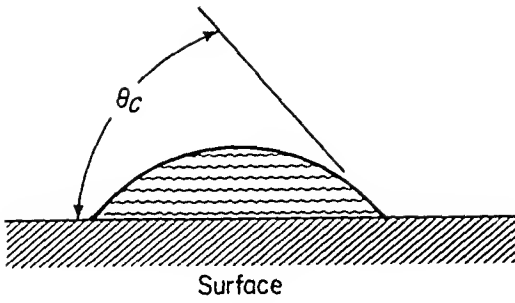


FIGURE 12-12
Definition of contact angle, θ_c , for liquid droplet on a surface.

metals are easily wetted by organic materials when they are clean. On the other hand, some liquids, upon contacting a surface, orient in such a way that the surface is converted to one more or less easily wetted than the original. Poly(dimethyl-siloxane) liquids have a surface tension of 19 to 20 dyn/cm (mN/m). However, a closely packed, adsorbed monolayer of the same polymer exhibits a surface of methyl groups with a critical surface tension of about 24 dyn/cm. Thus, silicones spread on almost all surfaces, since each surface, once wetted, is converted to one of higher surface tension than that of the liquid itself. Normal octyl alcohol also orients at a high-energy surface to convert it to a methyl surface. But now the surface tension of the alcohol (25 dyn/cm) is higher than that of the layer on the surface. Such a system is *autophobic*; i.e., spreading does not occur because the first molecules antagonize the surface.

If surfaces were perfectly smooth and clean, no adhesive would be needed. Almost any material cleaved in a high vacuum can be fused back together without an adhesive or high temperature. However, surfaces are rough on an atomic scale, and one of the functions of an adhesive is to fill in the asperities. Therefore all adhesives are applied as liquids. We can classify adhesives as being permanently liquid, solidifying by physical processes, or solidifying by chemical processes.

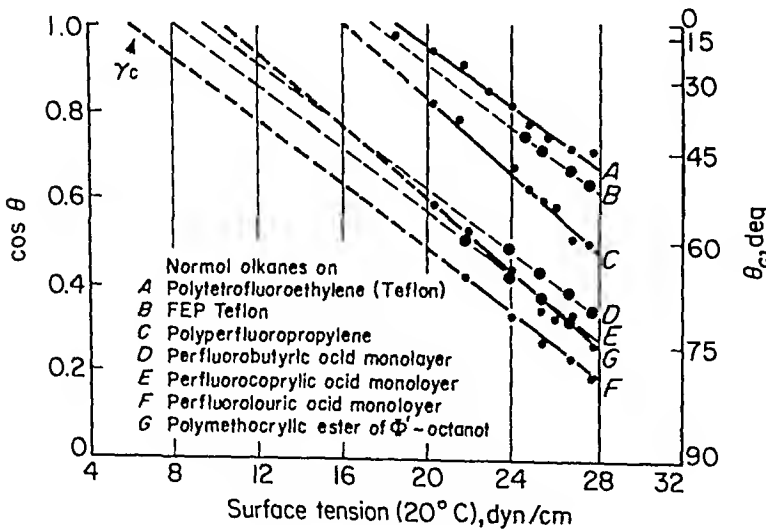


FIGURE 12-13
Contact angles formed by a series of liquid *n*-alkanes on various fluorinated low-energy solid surfaces [17].

TABLE 12-6
Critical Surface Tensions of Polymeric Solids [17] at 20°C

Polymeric solid	γ_c , dyn/cm (mN/m)
Polymethacrylic ester of Φ' -octanol*	10.6
Poly(hexafluoropropylene)	16.2
Poly(tetrafluoroethylene)	18.5
Poly(trifluoroethylene)	22
Poly(vinylidene fluoride)	25
Poly(vinyl fluoride)	28
Polyethylene	31
Poly(trifluorochloroethylene)	31
Polystyrene	33
Poly(vinyl alcohol)	37
Poly(methyl methacrylate)	39
Poly(vinyl chloride)	40
Poly(vinylidene chloride)	40
Poly(ethylene terephthalate)	43
Poly(hexamethylene adipamide)	46

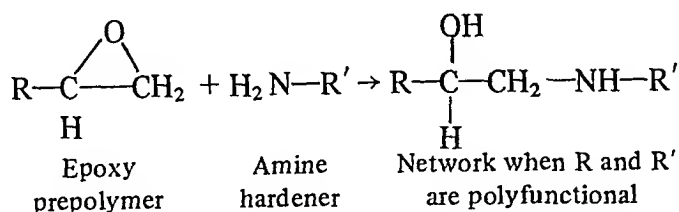
* Φ' -Octanol is $\text{CF}_3 \cdot (\text{C}_2\text{F}_2)_3 \cdot \text{CH}_2\text{OH} \cdot \text{CH}_2\text{OH}$.

Water is a good example of a liquid adhesive for almost any two surfaces. Its volatility, low viscosity, and high surface tension make it a poor adhesive, although when it freezes, it can be a very strong adhesive—as someone who has put his tongue on a frozen sled runner can attest. A plasticized rubbery polymer has low volatility, high viscosity, and low surface tension and makes a good adhesive. The common cellophane tape is a typical application of such a *pressure-sensitive* adhesive. The material remains permanently liquid but forms a strong bond between the surface and the cellophane backing when slight pressure is applied to cause flow. When the surface is paper, presumably both specific and mechanical adhesion may be involved.

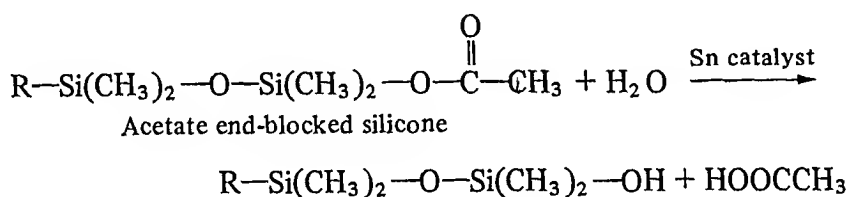
Tar and sealing wax are examples of adhesives that solidify by cooling after being applied as hot liquids. Some animal glues and thermoplastic resins are similarly applied. Most adhesives are counterparts of the coating systems we have already discussed. Model airplane cement is a polymer solution, often cellulose nitrate in a mixture of ketones and aromatic solvents. As a coating we would call it a lacquer. Aqueous solutions of natural and synthetic gums are used in library paste. Some of the popular white glues for paper and wood are simply poly(vinyl acetate) emulsions with a small amount of plasticizer. All of these materials solidify after contacting the surface as a liquid by loss of solvent or diluent. Evaporation or diffusion into a porous substrate may be involved.

The stronger adhesives generally are those that are thermosetting. They are applied as liquids but form network polymers by chemical reaction. It may be necessary to heat the liquid to cause the reaction to occur. A common system involves mixing two ingredients that will react after an induction period. The *pot life* of such a system is the time between mixing and conversion to a high viscosity unsuitable for spreading. Plaster of paris is a slurry of calcined calcium sulphate in water. The hardening reaction involves both hydration and crystallization. The epoxy resins can be

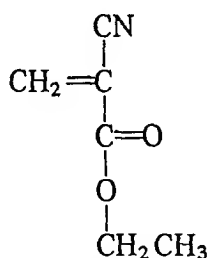
formulated so that the reaction between the epoxy prepolymer and the amine "hardener" (both polyfunctional) takes place 15 to 30 min after the mixing. Not every



reactive adhesive is made by mixing two ingredients. The RTV (room temperature vulcanizing) silicones are stable pastes for months as long as they are protected from the atmosphere. Exposure to a humid atmosphere brings about hydrolysis of acetate ester groups. In the presence of certain catalysts the SiOH groups condense to form Si—O—Si bonds.



The cyanoacrylate adhesives were introduced in the late 1950s. Unlike the epoxy or silicone adhesives, these materials contain a monomer that undergoes rapid polymerization at room temperature. The monomer ethyl cyanoacrylate is stable with trace amounts of an acid inhibitor such as polyphosphoric acid. The commercial formulations may contain methyl and higher cyanoacrylate esters, thickeners such as



Ethyl cyanoacrylate

organic polymers, and plasticizers for increased final film toughness. A slightly basic surface is needed for ionic polymerization to occur. Even the surface moisture of an ostensibly "dry" metal or ceramic surface is sufficiently basic. A really acid surface does require an alkaline pretreatment. The reaction time for polymerization is less than 10 s when a thin layer of monomer is applied to a clean, dry, smooth surface. A variety of cyanoacrylate adhesives are on the market with numerous brand names that convey the rapidity of bonding, the "superstrength" of the bond, or merely the imagination of a sales organization. Repairs of china, glass, plastics, and metals all can be quite dramatic as demonstrated in TV ads. However, the cyanoacrylates also have been used as sutures to glue together skin or other body tissues, as dental ad-

adhesives, and in industrial applications such as attaching ornaments in automobiles and in assembling electronic devices.

12-5 TWO-DIMENSIONAL PROCESSES

Extrusion in General

In *extrusion* a material is forced through a *die* that shapes the profile. Continuous flow of material results in a long shape of constant cross section. Unlike the extrudate from a toothpaste tube or a meat grinder, plastic extrudates generally approach truly continuous formation. They may attain dimensional stability in various ways. Like the usual meat grinder, the extruder (Fig. 12-14) is essentially a screw conveyor carrying cold plastic pellets forward and compacting them in the compression section with heat from external heaters and from the friction of viscous flow. The pressure is highest right before the plastic enters the die that shapes the extrudate. The screen pack and breaker plate between the screw and the die filter out dirt and unfused polymer lumps. When thermoplastics are extruded, it is necessary to cool the extrudate below T_m or T_g in order to gain dimensional stability. In some cases this can be done by simply running the product through a tank of water or, even more simply, by air-cooling. When rubber is extruded, dimensional stability comes about by cross-linking (vulcanization). Special attachments for continuous vulcanization are described later. Actually, rubber extrusion for wire coating was the first application of the screw extruder. The first extruder in the United States was built in 1880 by John and Vernon Royle, although some machines may have been in use in England as early as 1866 [19].

Standard sizes of single-screw extruders (specified by the inside diameter of the barrel) are $1\frac{1}{2}$, 2, $2\frac{1}{2}$, $3\frac{1}{4}$, $3\frac{1}{2}$, $4\frac{1}{2}$, 6, and 8 in. Smaller sizes are available for laboratory evaluations. As a rough guide, extruder capacity Q_e in pounds per hour, varies with the barrel diameter D_b , in inches, to the 2.2 power [20]:

$$Q_e = 16D_b^{2.2} \quad (12-1)$$

Another guide to extruder capacity stems from the fact that most of the energy that melts the thermoplastic results from mechanical work. The barrel heaters serve mainly to insulate the material. Allowing for an efficiency from drive to screw of about 75%, the capacity then depends on the power supplied H_p (horsepower), the heat capacity of the material c_p , (Btu/lb·°F), and the temperature change from feed to extrudate ΔT (°F):

$$H_p = 5.3 \times 10^{-4} Q_e c_p \Delta T \quad (12-2)$$

For example, a 10-hp motor on a 2-in extruder might be used for poly(methyl methacrylate), for which c_p is about 0.6 Btu/lb·°F. Formula 12-1 gives $Q_e = 74$ lb/h. Equation (12-2) indicates that $\Delta T_{\max}$ would be 430°F. In actual practice, a ΔT of 350°F would usually be adequate for this polymer. The same calculation is, of course, much simpler in SI units. For example, if a 10-kW motor delivers 75% of its energy to a

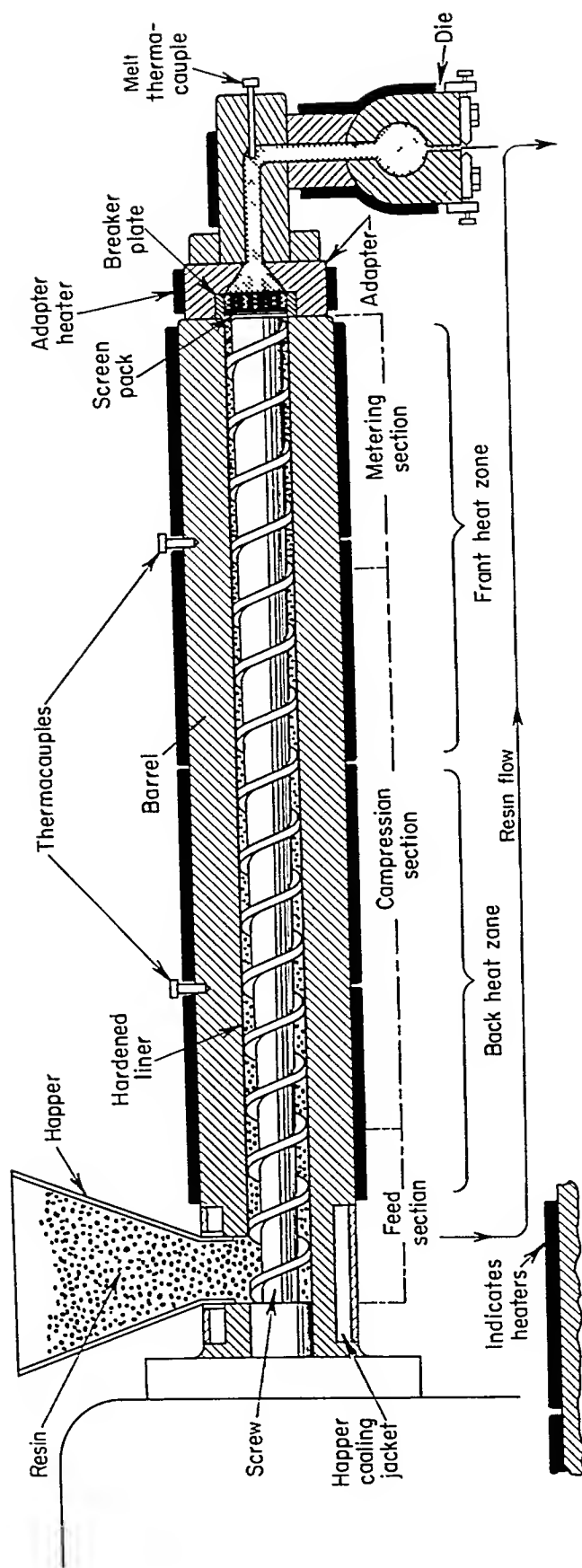


FIGURE 12-14
Cross section of a typical extruder [18].

throughput of 10 g/s of polymer with a heat capacity of $2.5 \text{ J/g}^\circ\text{C}$, the temperature change is

$$\Delta T = \frac{7500 \text{ J/s}}{(10 \text{ g/s})(2.5 \text{ J/g}^\circ\text{C})} = 300^\circ\text{C}$$

Obviously, these are very rough guides, since both polymers and machines are variable. Also, we have ignored the heat of melting and other thermal effects.

Besides barrel diameter, the length to diameter ratio L/D of an extruder is most often specified. Ratios of 20:1 and 24:1 are common for thermoplastics. Lower values are used for rubber. A long barrel gives a more homogeneous extrudate, which is especially important when pigmented materials are handled. A popular variant of the standard single-screw extruder is the vented model. Even when polymer pellets are predried, the compacting process may trap air bubbles in the melt. By placing an obstruction in the barrel (the reverse flights in Fig. 12-15) the pressure on the melt can be reduced suddenly to that of the atmosphere. Since the polymer does not have to be remelted, the feed section does not have to be replicated in the remainder of the screw. Valves can be used to adjust the pressure in various sections of the barrel. Although many screw designs are available, most have three zones, which differ in channel depth but not in pitch (which is synonymous with lead, since we are dealing with a single thread) (Fig. 12-16). The ratio of channel depth in the feed section to that in the metering section, the *compression ratio*, probably would best be adjusted to each polymer and each temperature used in a given machine. However, it is seldom feasible to stock more than two or three screws for a single extruder, so a compromise is made. Some considerations would be (1) the form in which polymer is to be fed to the machine, i.e., pellets, powder, continuous ribbon; (2) the melt viscosity; and (3) thermal degradation. One screw might be suitable for polyethylene and ABS polymers, another for polyamides with their characteristic low melt viscosities, and another for poly(vinyl chloride) or poly(vinylidene chloride), each of which degrades easily at elevated temperatures. In laboratory-sized equipment one might extrude a filled rubber by using still another screw. However, since rubber usually is fed as a warm ribbon, it has to be cooled to prevent cross-linking in the barrel, and then must be heated to cross-link subsequent to extrusion; it becomes apparent that production

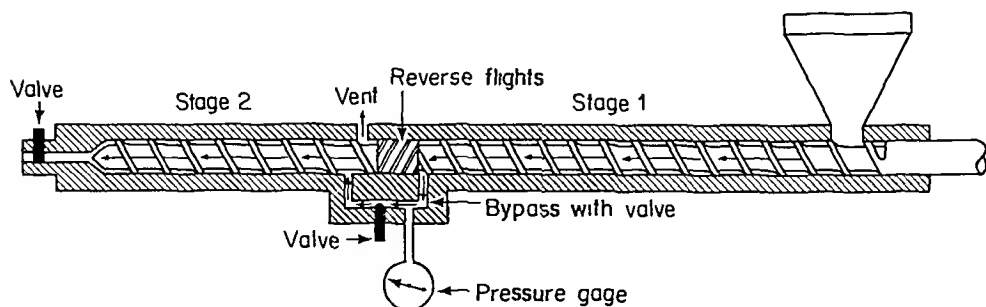


FIGURE 12-15

A two-stage vented extruder in which a valved bypass section steps down the pressure developed in the first stage to atmospheric pressure for venting; valve is for adjustment [20].

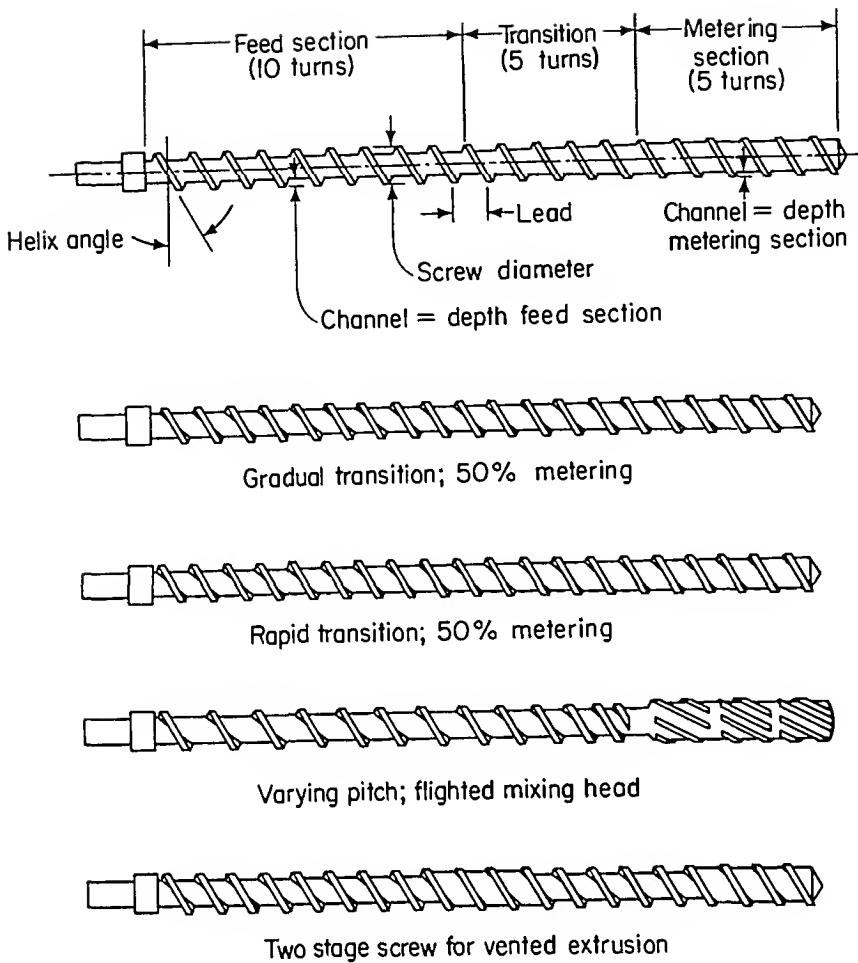


FIGURE 12-16

The various zones or sections of a standard constant-pitch, rapid-transition, metering extruder screw are labeled in the above drawing [20]. Some other designs are shown also.

machinery that attempts to do all this and still be versatile enough to handle thermoplastics probably will be inefficient for both.

Twin-screw extruders may have the two parallel screws rotating in the same direction. Another form has counter-rotating screws with some meshing to give a conveying action similar to a positive displacement pump. Some advantages generally claimed for twin-screw over single-screw extruders are better control, lower possible melt temperatures, and better mixing. These advantages must be weighed against a higher initial cost. Some other features of extruders are best described in terms of specific shapes.

Flat Film, Sheet, and Tubing

By definition the term *film* is used for material less than 0.010 in thick and *sheet* for that which is thicker. Since the material will issue from the extruder as a thin unsupported web of molten polymer, it is obvious that a high melt viscosity and some elasticity are desirable. The most direct control for these parameters is the molecular weight distribution. Often a polymer blend will perform better than a single component. *Flat-film* extrusion uses a T-shaped die (Fig. 12-17). The die opening for

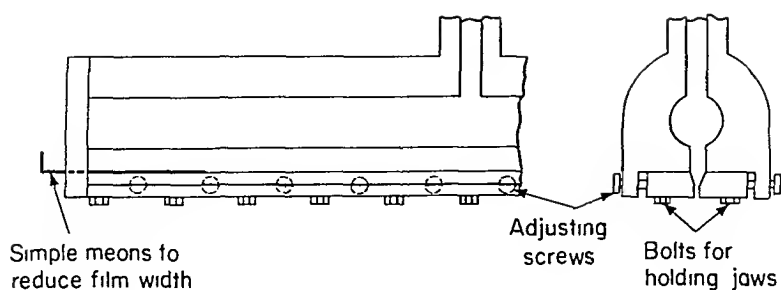


FIGURE 12-17

Schematic drawing of a manifold-type flat-film die with adjustable jaws [18].

polyethylene may be 0.015 to 0.030 in even for films that are less than 0.003 in thick. The speed of taking up the film (various driven rolls) is high enough to draw down the film with a concurrent thinning. Dies may be as wide as 10 ft. On leaving the extruder the film may be chilled below T_m or T_g by passing through a water bath or contacting a water-cooled roll. A schematic drawing of a *chill-roll* (also called *cast-film*) operation (Fig. 12-18) shows how the hot web is made dimensionally stable by contacting several chrome-plated chill rolls before being pulled by the driven carrier rolls and wound up. The edges of the sheet may be trimmed off, since some curling occurs there. The draw-down process (followed by cooling before relaxation can occur) results in an oriented film whether the polymer is glassy or crystalline. Thicker sheets generally are not drawn down as much and exhibit much less residual orientation. *Biaxially oriented* film can be produced from a flat web by using a *tenter* (Fig. 12-19). Polypropylene, for example, might be extruded as a web about 0.005 in thick from a slot die. Inside a temperature-controlled box, the web is grasped on either side by tenterhooks which can exert a drawing tension as well as a widening tension. Where hooks disengage the final sheet might be two or three times as wide as it was originally and, of course, considerably thinner. Biaxial orientation can be equal in two directions or unbalanced. In either case, molecules are now randomly oriented in two dimensions just as fibers

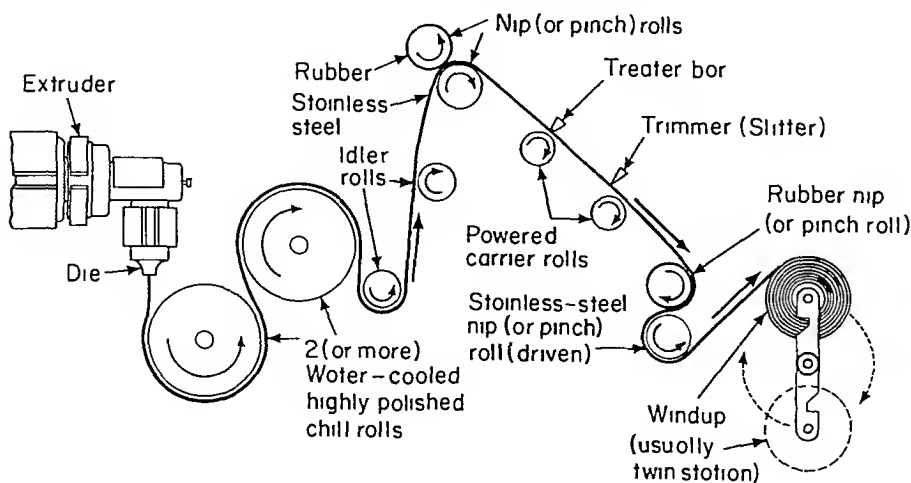


FIGURE 12-18

Schematic drawing of chill-roll film extrusion equipment [18].

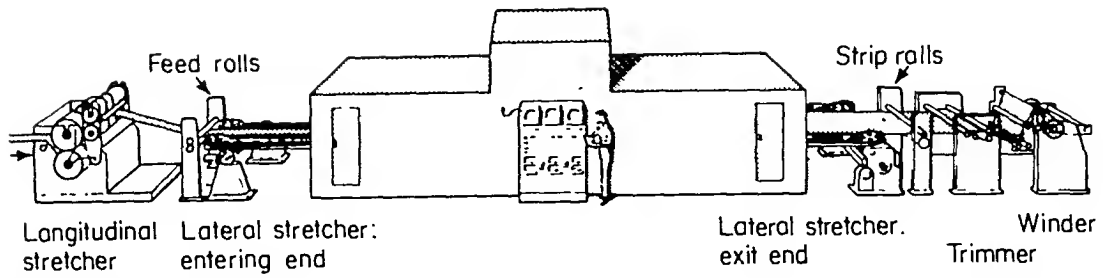


FIGURE 12-19

Biaxial orientation (tentering) of flat sheet in housing with programmed temperature [21].

would be in a random mat. With polyethylene, biaxial orientation often can be achieved in *blown-film extrusion*. The molten polymer (Fig. 12-20) is extruded through a ring-shaped die around a mandrel. The tube or sleeve so formed is expanded around an air bubble, is cooled to below T_m , and then is rolled into a flattened tube and wound up. Since the bubble is sealed at one end by the mandrel and at the other by the nip where the tube is flattened, air cannot escape and the bubble acts like a permanent shaping mandrel once it has been injected. Cooling of the film is controlled by an air ring below the bubble. When polyethylene cools, the crystalline material is cloudy compared to the clear amorphous melt, so the transition line, which coincides with dimensional stabilization, is called the *frost line*. The *blowup* ratio (bubble diameter/die diameter) may range as high as 4 or 5, although 2.5 is a more typical figure. Orientation occurs in the hoop direction during blowup. Orientation in the

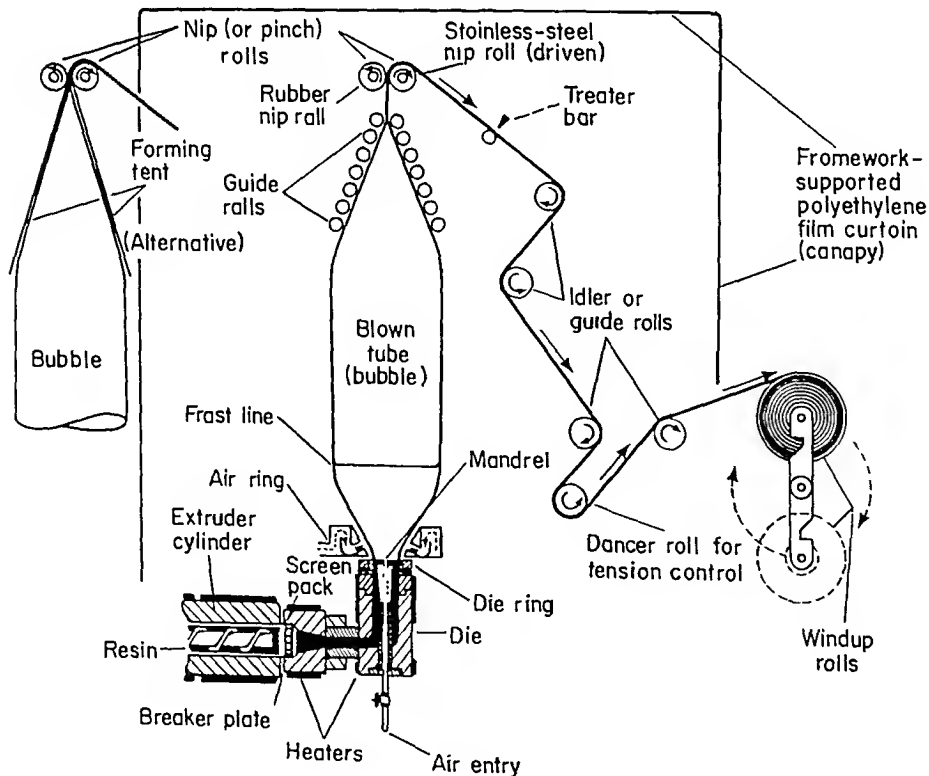


FIGURE 12-20

Schematic drawing of the blown-film extrusion process [18].

machine direction (in the direction of extrudate flow from the die) can be induced by tension from the nip roll. The method produces wide films used in construction trades as wind or moisture barriers. One example is reported as involving a 10-in extruder, a 5-ft diameter die, and a blowup ratio of 2.5 to give 1100 lb/h of polyethylene film, which when slit is 40 feet wide [22]. Such films in thicknesses of 0.004 to 0.008 in are readily available from hardware firms and mail-order companies for farm and construction applications. Nylon and poly(vinylidene chloride) are also produced by blow extrusion.

Pipe or tubing is extruded through a ring-shaped die around a mandrel. Because heavier walls are involved than in blown-film extrusion, it is advantageous to cool by circulating water through the mandrel (Fig. 12-21) as well as by running the extrudate through a water bath. The extrusion of rubber tubing differs from thermoplastic tubing, since dimensional stability results from a cross-linking reaction at a temperature above that in the extruder rather than by cooling below T_g or T_m . The high melt viscosity needed to ensure a constant shape during the cross-linking may be an inherent property of the rubber being extruded. More often, however, the addition of a filler will induce the same behavior. For example, 20 parts of finely divided silica added to 100 parts of a poly(dimethyl siloxane) will increase the apparent viscosity only about twofold at a rate of shear equal to 100 s^{-1} . The viscosity at a stress corresponding to the unsupported polymer is measurable for the unfilled material but essentially infinite for the filled polymer. It is possible to extrude a filled rubber through a ring die to give a tube with a 12 mm outside diameter and a wall thickness of 3 mm and to cross-link it continuously by carrying it through a radiant-heated tunnel on a steel conveyer belt. With a residence time of 10 s in a 6-m-long tunnel, the tubing emerges with very little sagging of the original circular cross section.

Almost any cross section can be extruded. A complication is the swelling of the polymer when the elastic energy stored in capillary flow is relaxed on leaving the die. The flat sheet or circular cross sections discussed so far are not sensitive to this *die swell* (Sec. 7-8), since the shape remains symmetrical even though the extrudate dimensions differ from those of the die. Also, the tension exerted on the extru-

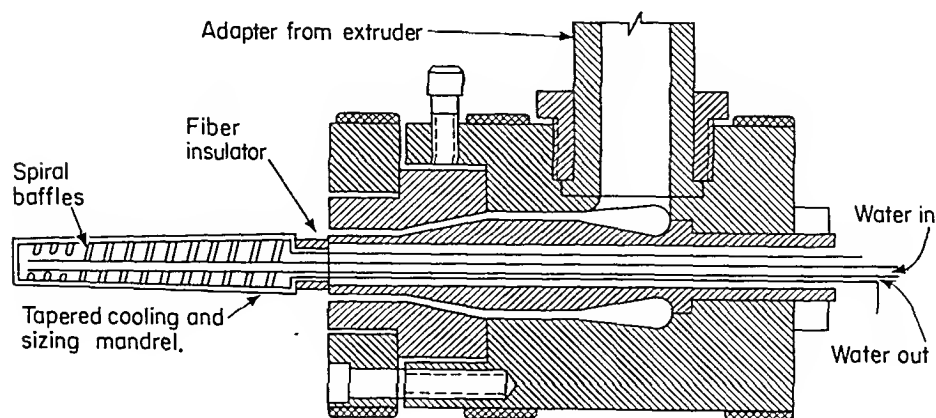


FIGURE 12-21

A tapered cooling and sizing mandrel is used in this extrusion die, which is designed for use in producing either pipe or tubing [20]. (Courtesy of Union Carbide.)

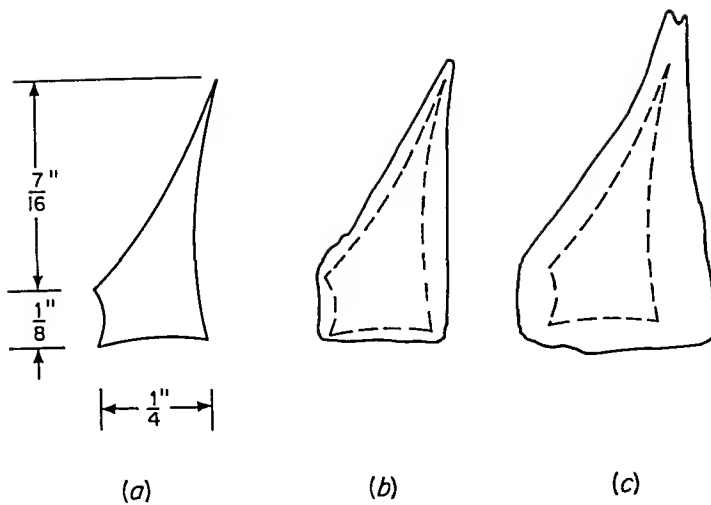


FIGURE 12-22
Garvey die for judging extrudate quality. (a) Die dimensions (and dimensions of ideal extrudate); (b) marginal extrudate showing swelling and some distortion; (c) badly distorted extrudate.

date can be used to counteract the swelling. Unsymmetrical cross sections may be distorted as the result of die swell. A standard test in the rubber industry gives a qualitative answer to the question of suitability for a given compound and machine setting. Extrusion through the peculiarly shaped Garvey die (Fig. 12-22) is sensitive both to die swell (shown by rounded corners and convex surfaces) and other irregularities that may occur because of poor cohesion or poor surface lubricity [23]. The maximum rate at which even a symmetrical cross section can be extruded generally will correspond to the flow rate region of “melt fracture” or some other kind of periodic flow distortion. Die entrance geometry and temperature control may affect the extrudate as well as the usual variables of composition.

A particularly clever mechanical arrangement permits the extrusion of a continuous sleeve of loosely knitted fibers suitable for being made into bags of the sort used for onions and potatoes. Two elements that rotate concentrically (Fig. 12-23) bear hemicylindrical slots through which the polymer melt is pumped. When the slots coincide, the filaments being extruded converge and are welded together. With a die like that in Fig. 12-23, 16 threads are extruded, 8 of them convex outward and 8 in toward the axis about which the elements rotate.

Another intriguing process also uses counterrotating dies. Two polymers are fed between the dies in the manner suggested by Fig. 12-24. As the dies rotate, the two polymers are stretched out laterally into a multiplicity of layers. In one example [25], poly(methyl methacrylate) and polystyrene are made into a tube with over 100 layers. Combined with blown-film extrusion, a film only $25\text{ }\mu\text{m}$ thick can be made with individual layers having thicknesses near the wavelength of visible light. Very attractive diffraction patterns are produced, which suggest the use of the film in decorative applications. An iridescent film based on propylene and polystyrene has been available commercially since 1976 [26]. Some uses for it include overwraps for cosmetics and toiletries, gift wrapping, and wallcoverings.

The application of insulation to a continuous length of conductor represented one of the first uses of extruders for rubber about 100 years ago and also one of the

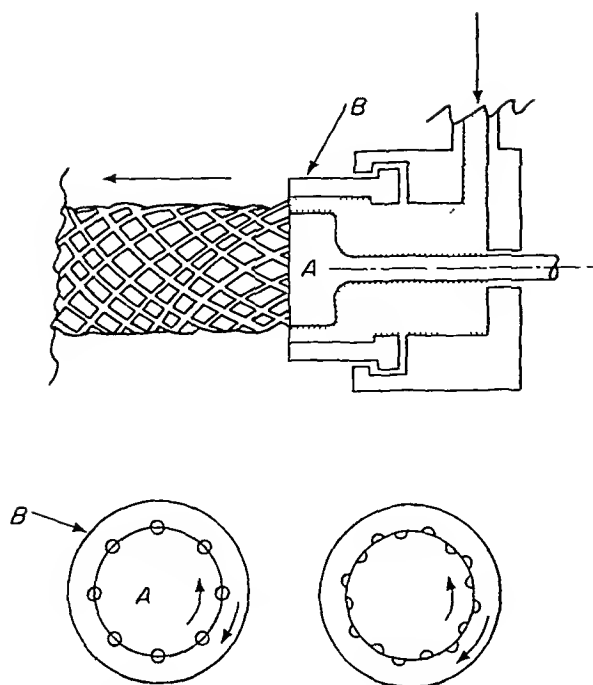


FIGURE 12-23

Rotating dies for extrusion of net material [24].

first uses with thermoplastics in the 1930s. The process resembles that used for pipe with extrusion around a mandrel except for the drawing of the conductor through the mandrel on a continuous basis. For thermoplastics such as polyethylene, nylon, and plasticized poly(vinyl chloride), a slight downward pitch from the extruder into a water trough is enough to cool the insulation below T_m or T_g . At the far end of the trough the wire or cable with its hardened insulation can be withdrawn under tension around a pulley or drum, dried, and wound up. The conductor is not always a single metal strand. It can be a multiple strand or even a bundle of previously individually insulated wires. Cloth or paper may have been wrapped around the bundle in a previous stage also. With rubbers that have to be cross-linked by heating subse-

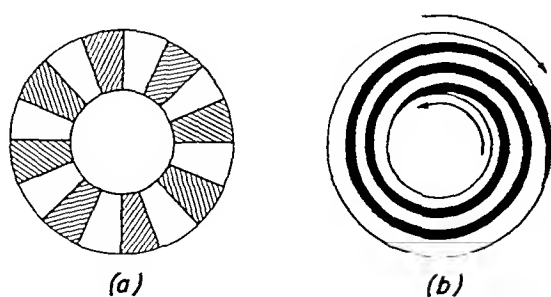


FIGURE 12-24

Production of multilayered sheet by extrusion. (a) Head-on view of two polymers entering an annular die like spokes on a wheel. (b) Spiral formation of multiple layers by a single spoke between counter-rotating dies.

quent to extrusion, several routes are available. If the insulation has high dimensional stability, the un-cross-linked extrudate may be coiled up and the entire assembly heated in a pressurized, steam-heated tank. The hot-air vulcanization mentioned previously for silicone tubing is feasible. Higher heat transfer rates and less porosity than the hot-air tunnel are obtained by vulcanizing in high-pressure steam. The CV (continuous vulcanizing) process puts the coated conductor through as much as several hundred feet of pipe containing steam at up to 250 psig (1.7 MPa). By extruding vertically downward, the sagging of the insulated wire is avoided (Fig. 12-25). The seal at the upper end is obtained by butting the pipe against the extruder head. The bottom 3 m of the pipe contains cooling water, which hardens the now cross-linked insulation somewhat and allows the cable to be withdrawn through a seal without damaging the coating.

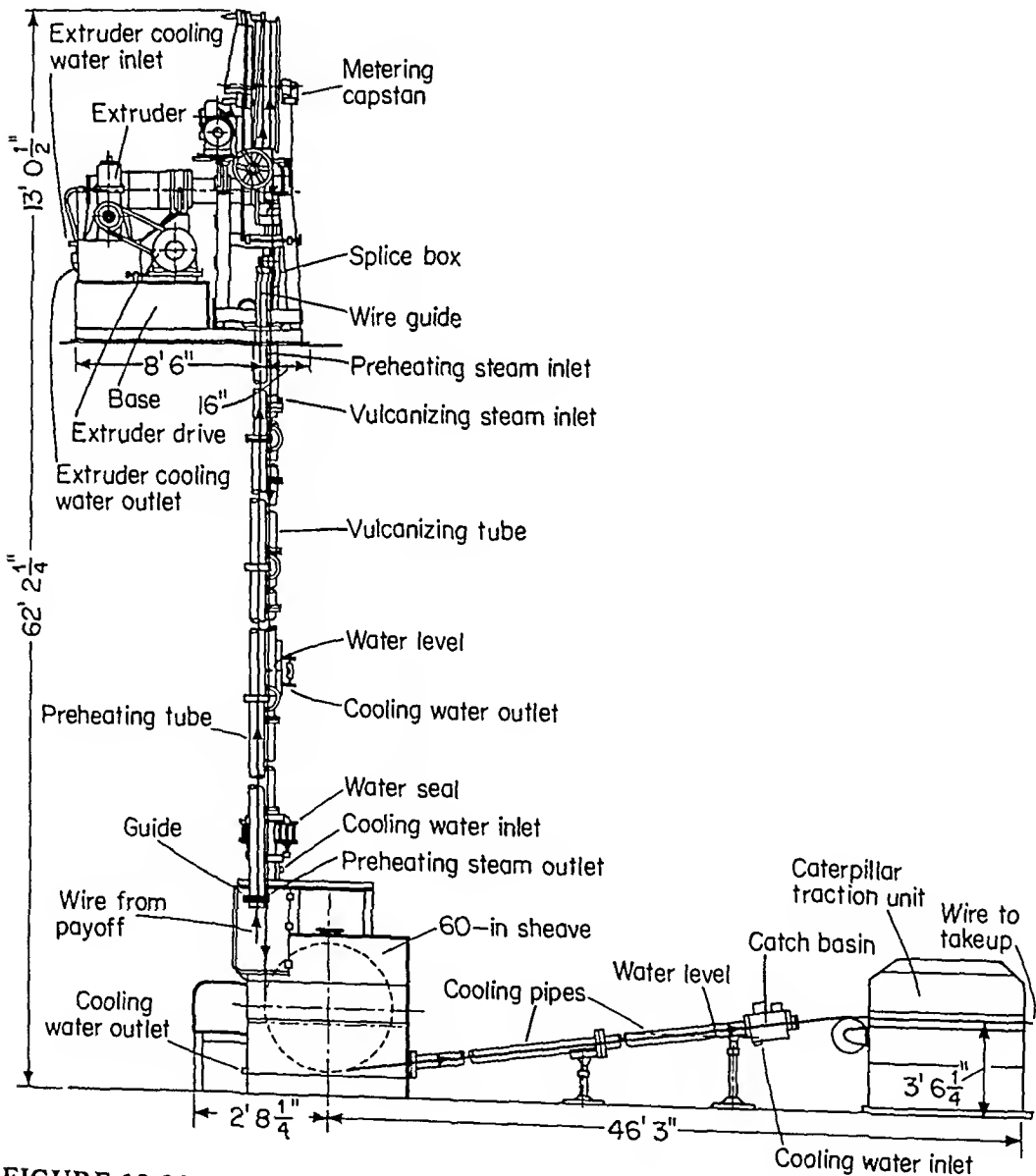


FIGURE 12-25

Vertical continuous vulcanizer. Extruder is near the top of the assembly. (Fawcett Davis-Standard, Davy Plastics Machinery, Ltd.) [27].

Pultrusion is a continuous molding process resembling the application of insulation to wire and cable (Fig. 12-26). Typically, a glass fiber or fabric reinforcement is fed continuously from a spool through a resin bath. The resin-impregnated reinforcement is then pulled through a die that forms the desired cross-section and heats the material to start a "curing" reaction. If the resin is a mixture of styrene monomer and unsaturated polyester with a peroxide initiator, heating causes a free-radical copolymerization to occur. After emerging from the die the pultruded shape may be further heated by radio-frequency energy (see Sec. 10-6). Some standard shapes produced by this process are angles, channels, I-beams, and tubes, as well as table legs and platforms [28].

Extruders are used as auxiliary equipment in many other kinds of forming operations. Pellets for thermoplastic molding are made by chopping the cylindrical "spaghetti" extruded through a multidie extruder head. The feed for a calender (see below) may come from an extruder. The thin film for a flat-film extruder may be directly laminated onto cardboard or another polymer film. Finally, a vented extruder can be used to dry a product or remove residual monomer from a polymer in an intermediate stage of production.

Two methods of producing flat films that do not involve extrusion should be mentioned. Most of the cellulose acetate (or acetate-butyrate) film that is coated with a gelatin emulsion for photographic purposes is produced by depositing a polymer solution (dope, lacquer) on a large drum and evaporating the solvent. In a typical installation the drum might be 4 ft wide and 18 ft in diameter. The solution is introduced at the top from a flow box, and by the time the wheel has turned about 300° (say 15 or 20 s), enough solvent has evaporated that the web is self-supporting and can be carried on to further drying and conditioning [29]. The alignment and polishing of the drum are very critical, because the thickness of the photographic emulsion to be added later on will reflect any variations in the film base material. Continuous metal belts also have been used, although control of film thickness is more difficult. Associated with this kind of operation is an elaborate solvent recovery system without which it is uneconomical.

Calenders resemble the two-roll mill (Fig. 12-3), except that three to five rolls may be used and they all rotate at the same speed. The action is essentially that of a

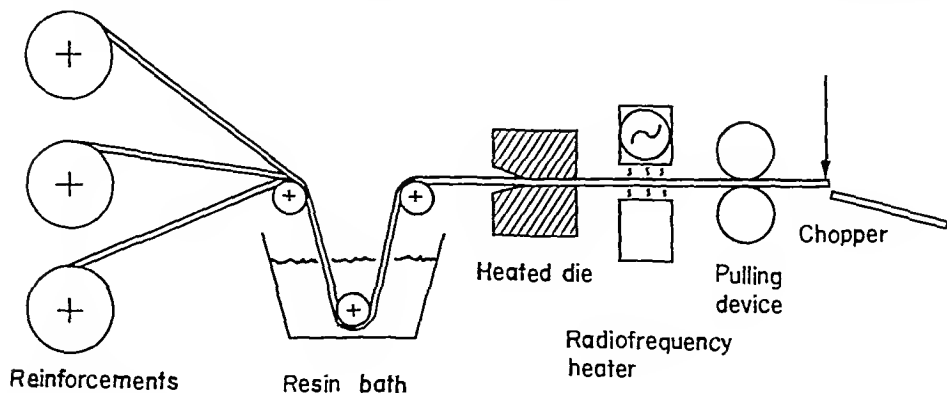


FIGURE 12-26
Pultrusion.

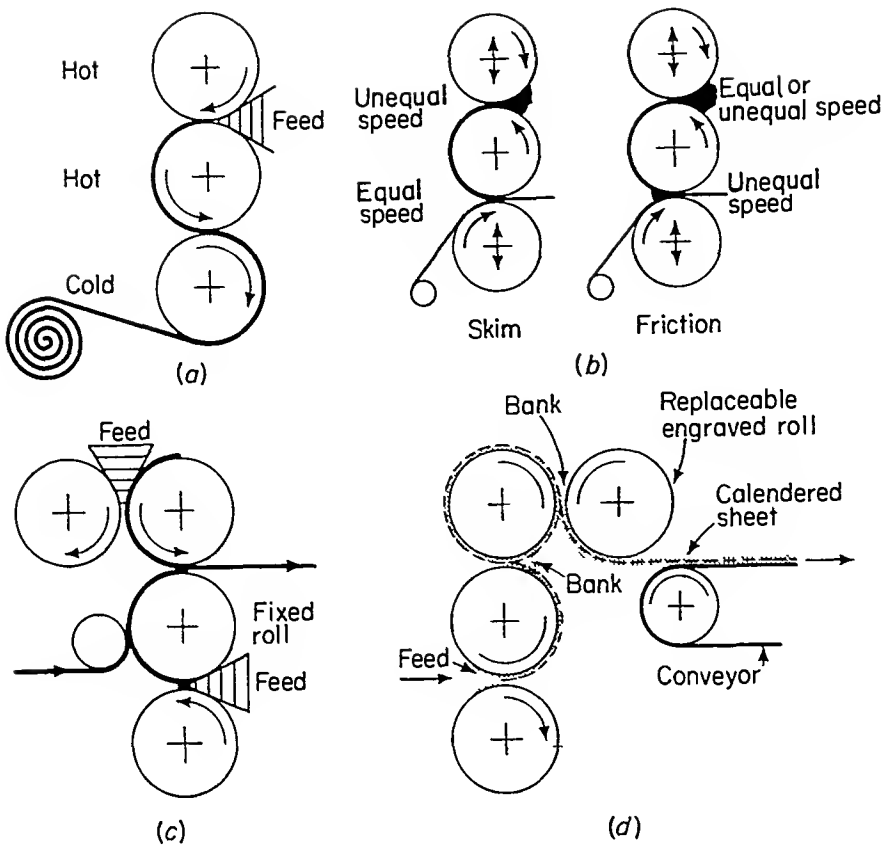


FIGURE 12-27
Calendering of rubber and plastics [30]. (a) Single-ply sheeting; (b) applying rubber to fabrics; (c) double-ply sheeting; (d) profiling: four-roll engraving calender.

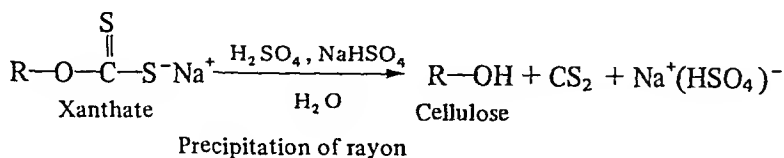
rolling pin or washer wringer. The material fed to the calender is usually preheated and may come directly from an internal mixer or an extruder. The calender squeezes the mass into a film or sheet, usually at an elevated temperature, and imparts a surface gloss or texture. Embossed or printed patterns are added on subsequent rolls. Some variations are shown in Fig. 12-27. Thick sections of rubber can be made by applying one layer of polymer upon a previous layer (*double plying*) or onto cloth fabric. Most plasticized poly(vinyl chloride) film and sheet from the 0.1-mm film for baby pants to the 2.5-mm “vinyl” tile for floor coverings is calendered. With thermoplastics the cooling below T_g or T_m can be accomplished on the rolls with good control over dimensions. With rubber, cross-linking can be carried out with the support of the rolls, once again with good control. It is only fair to point out that despite the simple appearance of the calender compared to the extruder, the close tolerances involved and other mechanical problems bring the cost of a calendering line to about a million dollars.

Fibers [31–33]

The term *spinning* as used with the natural fibers (and with the spinning wheel of colonial days) refers to the twisting of short fibers into continuous lengths. In the modern synthetic fiber industry the term is used to denote the process of producing continuous lengths by any means. First, we should define several other terms [34].

A *fiber* is the fundamental unit of textiles and fabrics and can be defined as a unit of matter having a length at least 100 times its width or diameter. A *filament* is an individual strand of continuous length. *Yarn* may be formed by several processes. Continuous filament yarn, as the name implies, is made by twisting together filaments into a strand. If the filaments are assembled in a loose bundle, we have *tow* or *roving*, which can be chopped into lengths of *staple* (an inch to several inches long). *Spun yarn* is made by twisting (plying) the lengths of staple into a single continuous strand. *Sewing thread* is a variety of yarn that is plied and then finished to give a smooth, compact strand. *Cord* is formed by twisting together two or more yarns. In the production of synthetic fibers the primary fabrication process of interest is the formation, "spinning," of filaments. In every case a polymer melt or solution is put in filament form by extrusion through a die. Usually the *spinneret*, the element through which the polymer is extruded, has a multiplicity of holes. Some rayon spinnerets have as many as 10,000 holes in a 15-cm-diameter platinum disc. Textile yarns might be spun from spinnerets with 10 to 120 holes and industrial yarns such as tire cord from spinnerets with up to 720 holes. Three major categories of spinning processes are used, melt, dry, and wet spinning [33].

Melt spinning is the same as melt extrusion. A polymer with a high melt viscosity such as polypropylene may be converted into a fiber by using a screw extruder to feed a heated spinneret with subsequent cooling under tension. Nylon, which has a lower melt viscosity, is fed to the spinneret through a gear pump (Fig. 12-28). *Dry spinning* also uses a pump to feed a polymer solution to a spinneret. Dimensional stability now involves evaporation of solvent as in the film-casting process. Even when dried under some tension, the diffusion of solvent out of the partly dried fiber results in an uneven fiber formation. The skin that forms first on the fiber gradually collapses and wrinkles as more solvent diffuses out and decreases the diameter. The cross section of a dry-spun fiber characteristically has an irregularly lobed appearance (Fig. 12-29). Solvent recovery is important to the economics of the process. Cellulose diacetate dissolved in acetone and polyacrylonitrile in dimethyl formamide are two current examples. *Wet spinning* also involves pumping a solution to the spinneret. Now, however, the polymer is precipitated in an immiscible liquid. Polyacrylonitrile in dimethyl formamide, for example, can be precipitated by passing a jet of the solution through a bath of water, which is miscible with the solvent but causes the polymer to coagulate. Cellulose triacetate can be wet-spun from a methylene chloride-alcohol mixture into a toluene bath, where it precipitates. In other fibers the precipitation can involve a chemical reaction. Viscose rayon is made by regenerating cellulose from a solution of cellulose xanthate.



This process could be carried out with a slot die rather than a spinneret, in which case *cellophane* would be produced. A ring die would give a continuous tube used as

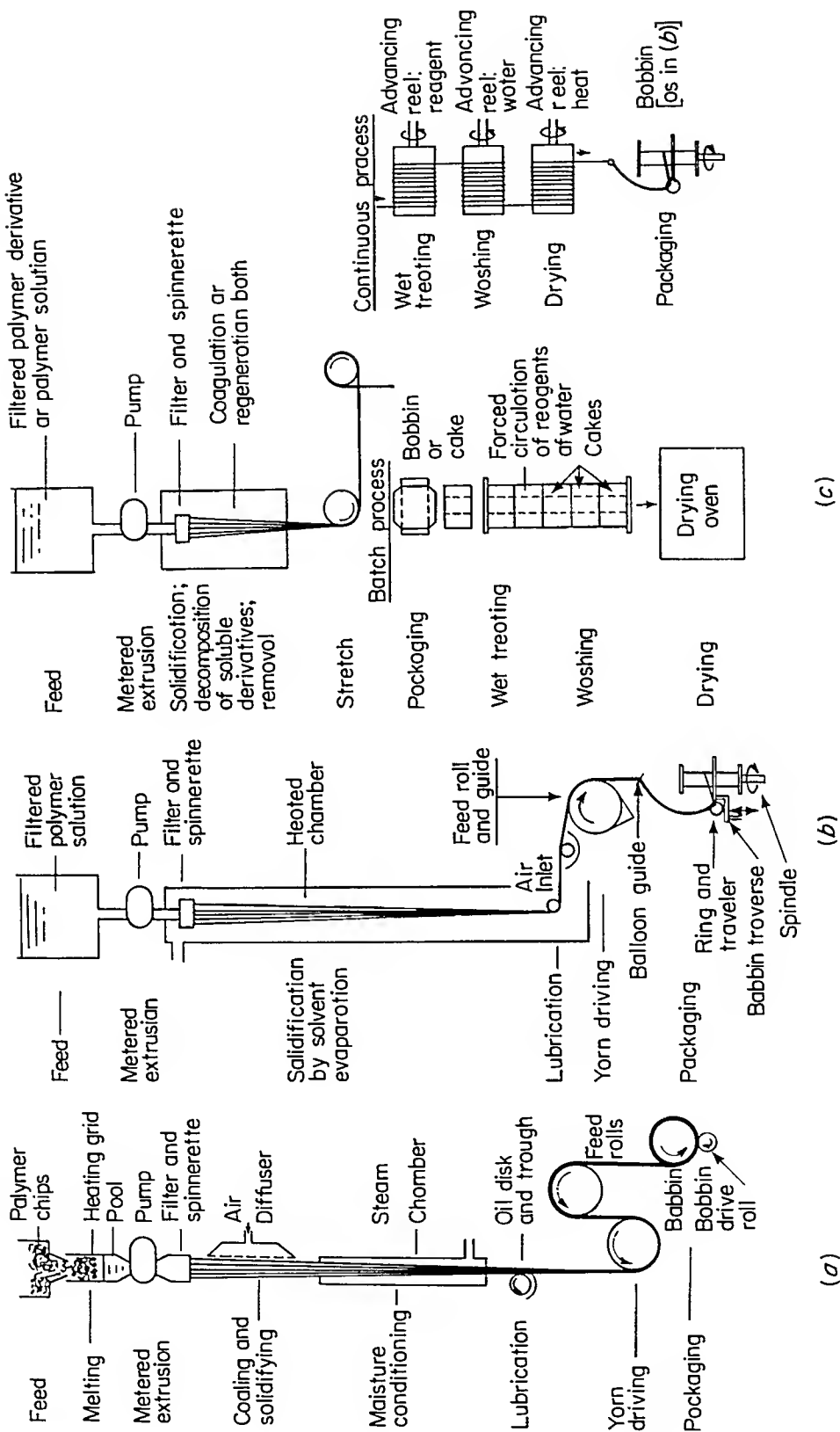


FIGURE 12-28 Features of the three principal types of fiber spinning. (Courtesy of Celanese Corp.) [33]. (a) Melt spinning; (b) dry spinning; (c) wet spinning.

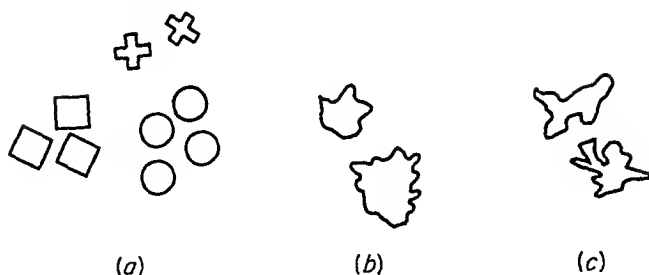


FIGURE 12-29

Typical cross sections of (a) melt-spun nylon from various shaped orifices, (b) dry-spun cellulose acetate from round orifice, and (c) wet-spun viscose rayon from round orifice.

sausage casing for the ubiquitous American hot dog. The casing is removed before final packaging of the “skinless” frankfurter.

Almost all synthetic yarns are so drawn that the crystalline structure is oriented in the direction of the fiber axis. Usually yarns are drawn at a temperature between T_g and T_m . The T_g may be depressed by the presence of a plasticizer, particularly water (Secs. 3-3 and 3-6). Some mechanical arrangements for continuously drawing yarn are shown in Fig. 12-30. In each case the drawing is accomplished by winding the yarn around a drum or wheel driven at a faster surface velocity than a preceding one. Polyethylene could be drawn, as indicated in Fig. 12-30a, at room temperature, whereas nylon 66 would have to be heated or humidified to be drawn. Fluted glass feed rolls called *godets* are used in Figs. 12-30b and 12-30c to control the speed of yarn. Many fibers are drawn as an integral part of the spinning process. In some cases it is preferable to store the fibers or carry out some other operation first, such as dyeing or twisting, and then to draw, in which case a plasticizing bath may be used to facilitate the process. In any case, the drawing does orient crystallites in the direction of the applied strain so that the modulus in that direction is increased and elongation at break is decreased.

The smooth cylindrical shape may not be the optimum one for apparel use. The seeming futility of chopping tow or roving into staple, only to respin the staple into a yarn, makes more sense when one sees the difference the operation makes in the apparent bulkiness of fibers in a sweater or blouse. Another means of increasing the bulkiness of yarn is to *crimp* the fibers by mechanical or other means. A simple means of inducing crimp (waviness) is to pass the fiber between two heated, fluted rolls or between two meshing gears (Fig. 12-31). More elaborate means of texturing yarns include twisting and untwisting, knitting and deknitting, and chemical treatments. Staple fibers often are textured before being chopped into staple.

In some applications it is desirable to have individual fibers that are very stiff. A column with a cruciform cross section is stiffer than one with a circular cross section (Fig. 12-29), and it is quite feasible to melt-extrude such shapes in polypropylene for rugs, for example. Hollow fibers can be produced in various ways. Discontinuous air cells increase the bulk of the fiber and can give some interesting handling properties causing some synthetics to resemble fine wool. By extruding around a mandrel, a continuous void can be formed inside a fiber. So-called hollow fibers are really small-size tubes. Bundles of such fibers are assembled into separators that

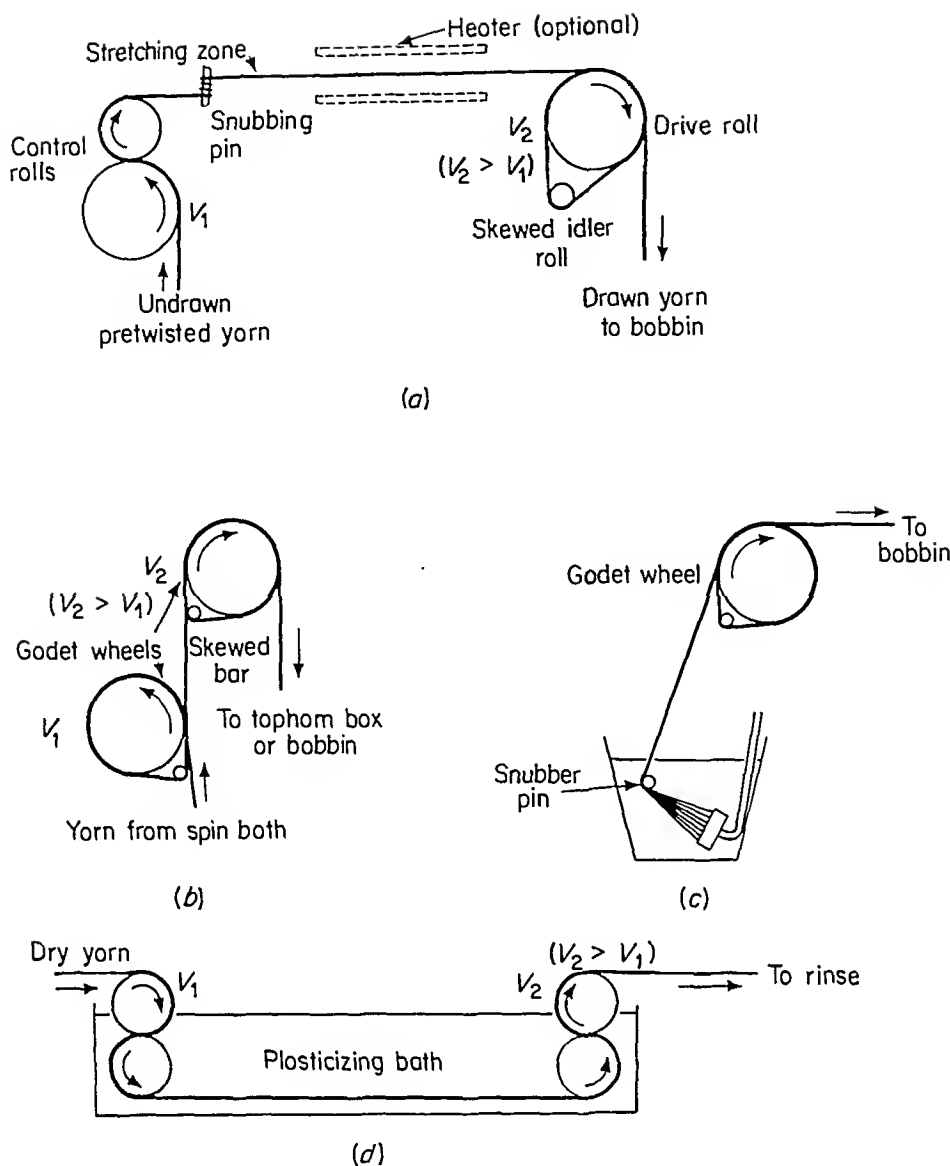


FIGURE 12-30

Four types of drawing processes used for synthetic fibers. V_1 and V_2 indicate relative velocities of take-up rolls (Courtesy of Celanese Corp.) [33]. The processes involve (a) cold (or hot) draw, (b) godet-controlled wet stretch of nascent yarn, (c) snubber-controlled wet stretch of nascent yarn, and (d) roll-controlled wet stretch of replasticized yarn.

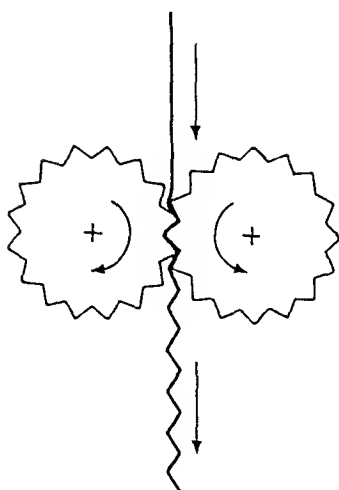


FIGURE 12-31

Mechanical crimping.

resemble shell-and-tube heat exchangers. The tubes act as semipermeable membranes. Such devices have been used for water desalination and as artificial kidneys. For separating hydrogen from gas streams, over 10,000 fibers (0.8-mm OD, 0.4-mm ID) may be packed into a shell that is 20 cm in diameter and 3 m long [35].

For many of the mechanical operations with fibers such as knitting and spinning, lubricants or other agents may be needed to prevent fouling of machinery. Printing and dyeing of textile fabrics is another large field in itself.

In recent years the application of thermosetting resins to fibers as wash-and-wear treatments has become a major industry. The general idea is to enhance the "memory" of the fabric for creases put in before setting the resin and to minimize subsequent wrinkling. Melamine and urea resins applied to cotton comprise one large class of such materials. Due to their comparatively hydrophobic nature, nylon and poly-(ethylene terephthalate) fibers do not require such treatment. While low moisture absorption is good for dimensional stability, it is often accompanied by low electrical conductivity. This brings on a second problem, that of static electricity. The charges on hydrophobic fibers do not leak off, and they cause apparel to cling uncomfortably. Also, most people have had the experience of walking across a deep-pile rug on a low-humidity, winter day and finding on reaching for the doorknob that a substantial difference in electrical potential has been induced between themselves and the knob. Finishes are available to counteract that static buildup too. In apparel the solution most often is to blend the nonconducting synthetics with the more conductive cotton or wool.

Laminates

In industrial terminology, laminates include many types of heterogeneous materials whether in layers or not. Here we shall restrict the term to standard shapes that are made in flat sheets of the same or different materials. A familiar example that illustrates the method and the advantages of lamination is plywood. Thin sheets of *veneer* are cut by knives whose blades stretch the length of a log and cut at an angle almost tangential to the curvature of the log surface. Such sheets are very strong in the direction of the tree axis and comparatively weak at 90° to that axis in the plane of the veneer. By plying the layers of veneer at right angles (usually with an odd number of layers), the strength can be made nearly equal in both directions. This makes the plywood superior to a board cut from the same wood provided the plies can be held together strongly. Phenol-formaldehyde resins are used to bond, and to a certain extent impregnate, the veneers. The conversion of the prepolymers to the final thermosetting form takes place when the assembly is in a press under high pressure. There are several other advantages of plywood over single boards besides equalizing the directional strength. The impregnation decreases the moisture pickup of the wood, so that there is less swelling in humid atmospheres. For decorative purposes plywood paneling can be made from inexpensive wood such as fir except for the top layer on one side, which might be a specially decorated material or an expensive, rather rare wood. It is also possible to build moisture barriers, flameproofing materials, or insulating layers into such panels by modifying the inner layers.

Paper layers are laminated with various resins to make materials useful in electrical applications as well as the decorative laminates that are best known by their trade

names such as Formica and Micarta. Kraft paper, about the weight used in shopping bags, is taken directly from rolls and run through a solution of melamine-formaldehyde prepolymer in a typical application. Driving off the solvent or drying out water leaves an impregnated sheet that can be handled easily, since the brittle prepolymer does not leave the surface sticky. As many as a dozen or more layers of impregnated paper are laid up. For decorative purposes, a printed rag or cloth paper is put on top and covered with a translucent paper layer. The entire assembly is heated between smooth plates in a high-pressure press to carry out the thermosetting reaction that binds the sheets together into a strong, solvent-resistant, heat-resistant surfacing material. For use in tabletops, countertops, and so on, the laminate, which is only about 1.5 mm thick, can be glued to a plywood base.

There are numerous standardized classes of industrial laminates available. They vary in the reinforcement and in the binder. Besides paper, the reinforcement might be woven or knitted cloth, most often cotton or glass but possibly wool, asbestos, nylon, or rayon. The binder can be phenolic, melamine, polyester, epoxy, or any one of a variety of thermosetting resins. One of the more important industrial applications of such laminates is as the base material for printed circuits.

The impregnated sheet materials can be wound on themselves or on a mandrel and heated in a press with curved surfaces to make rods or tubes. In any case, ultimate use of the laminates often involves machining operations. For this reason the ease with which a particular laminate can be sawed, drilled, or punched often has a bearing on its suitability for a given application.

Sandwich construction usually connotes assembly with one material for both surfaces and a second material in between. A core of foamed polymer covered by plywood or metal layers is very stiff without being very heavy and is a good insulator. Plywood surface with a foamed polystyrene core is available in 4- by 8- and 4- by 10-ft panels for quick assembly into small housing units. Surface and core can be varied to impart abrasion resistance, weathering resistance, flame resistance, or radiation resistance for particular applications.

When a thin layer of a tough thermoplastic such as plasticized poly(vinyl chloride) is laminated to a metal sheet, the bond may be strong enough that the laminate can be punched, cut, or shaped without parting the two layers. A pattern can be printed or embossed on the plastic before subsequent fabrication. Appliance cabinets and typewriter cases have been produced by shaping operations carried out on such materials.

Laminates can be produced during extrusion. A multilayered laminate made using rotating dies has already been mentioned. Coextruded film and sheet may combine two or three different polymers in a single product. Adhesion is enhanced by cooling the laminate directly from the melt rather than in a separate operation after the film components have been formed and cooled separately. In one form, flows from individual extruders are combined in a *flowblock* and then conveyed to a single manifold die. Because laminar flow must be maintained, all the polymer streams have to have about the same viscosity. Systems with up to seven layers are reported to be in operation [36]. There are various reasons for wanting multilayer films and sheets. A chemically resistant sheet can be combined with a good barrier to oxygen or water diffusion. A decorative, glossy sheet can be placed over a tough, strong material. Not

all combinations adhere equally well, so there are limits to the design of such structures. One commercial example is a four-layered sheet (ABS, polyethylene, polystyrene, and rubber-modified polystyrene) for butter and margarine packages. Another is an ABS, high-impact-polystyrene sheet, which can be thermoformed (see Sec. 12-6, Sheet Forming) to make the inside door and food compartment of a refrigerator [36].

12-6 THREE-DIMENSIONAL PROCESSES

Molding

In almost all molding operations, some pressure and perhaps heat is applied to make the polymer flow into a preferred form. Dimensional stability then is conferred by cooling or further heating. Thermoplastic materials have to be cooled below T_m or T_g before being removed from the mold. This means a sequence of heating, pressurized flow, and pressurized cooling. Thermoset materials and rubbers have to be heated long enough for some chemical reaction to occur that brings about a stable, network structure. The sequence here is heating, pressurized flow, and pressurized reaction. Although some thermosets are cooled before ejection from the mold, most can be ejected hot.

Compression molding of combinations of shellac, straw, and various waxes and pitches goes back at least to the 1860s. The simplest compression mold is the flash mold. The only pressure on the material remaining in the mold when it is closed (Fig. 12-32) results from the high viscosity of the melt, which did not allow it to escape. Since most rubbers have high melt viscosities, especially when filled, the flash mold is widely used for mechanical goods such as gaskets and grommets and also for shoe heels, tub and flask stoppers, doormats, and other familiar items. Most thermoset prepolymers (phenolic and melamine, for example) are brittle and powdery at room temperature but have a low viscosity when heated, although the viscosity rapidly increases as cross-linking occurs. A primitive *positive-pressure* mold can be made from a

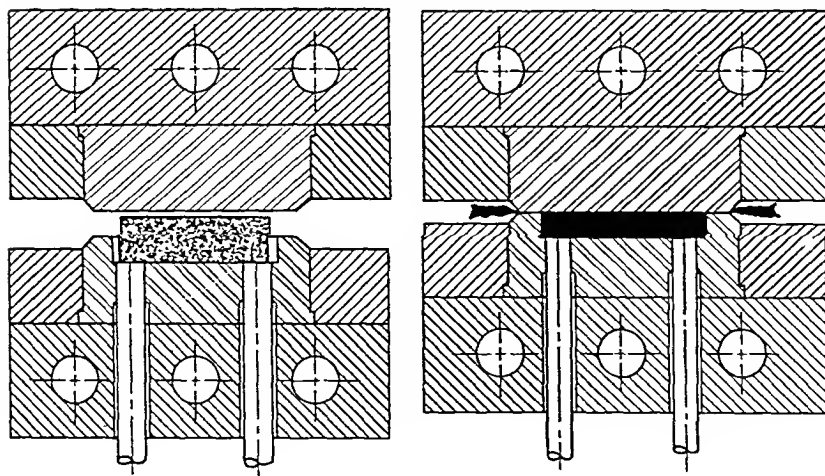


FIGURE 12-32

Flash mold: open, with preform in place, and closed, with flash forced out between mold halves [37].

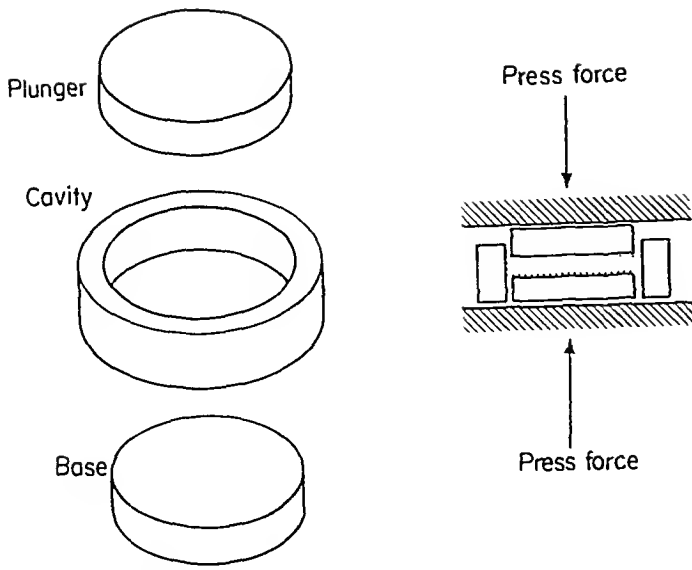


FIGURE 12-33
Elementary positive-pressure mold.

ring and two plates (Fig. 12-33). The final thickness of the molded disc varies with the amount of polymer charged initially. An *internally landed* semipositive mold (Fig. 12-34) exerts more pressure on the melt than the flash mold, but the final dimensions are controlled by the meeting of the plunger and a land, or shelf, on the cavity.

In either of the compression molds the prepolymer (molding powder) is melted and forced into the cavity simultaneously. If the polymer is being molded around a metal insert such as an electrical lug, the prepolymer may resist flow initially and exert a high force on the insert. In such a case it is desirable to melt the polymer in a separate operation and then inject it into the cavity. Because only seconds are available, both operations are carried out in the same equipment by *transfer molding*. The prepolymer is put into a pot in the mold (Fig. 12-35), from which it flows under the force of the plunger only after it has become hot enough to be rather low in viscosity. The material then is pushed into the cavity where it is held for the thermosetting

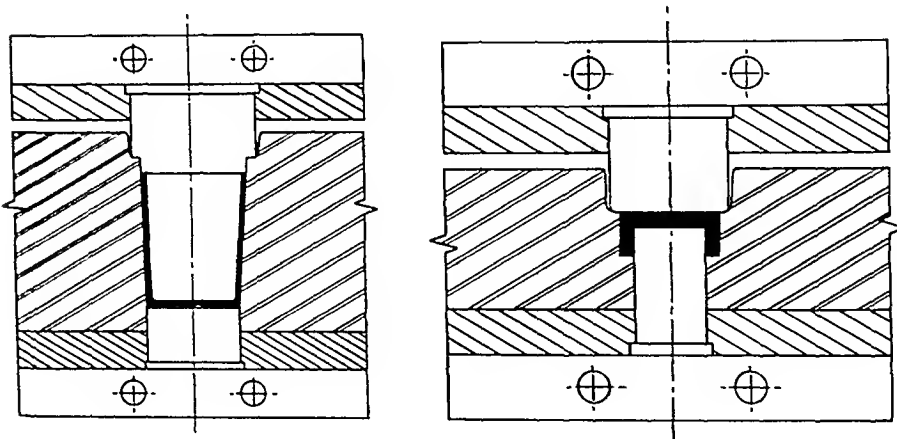


FIGURE 12-34
Internally landed positive and semipositive molds (both shown in closed position) [37].

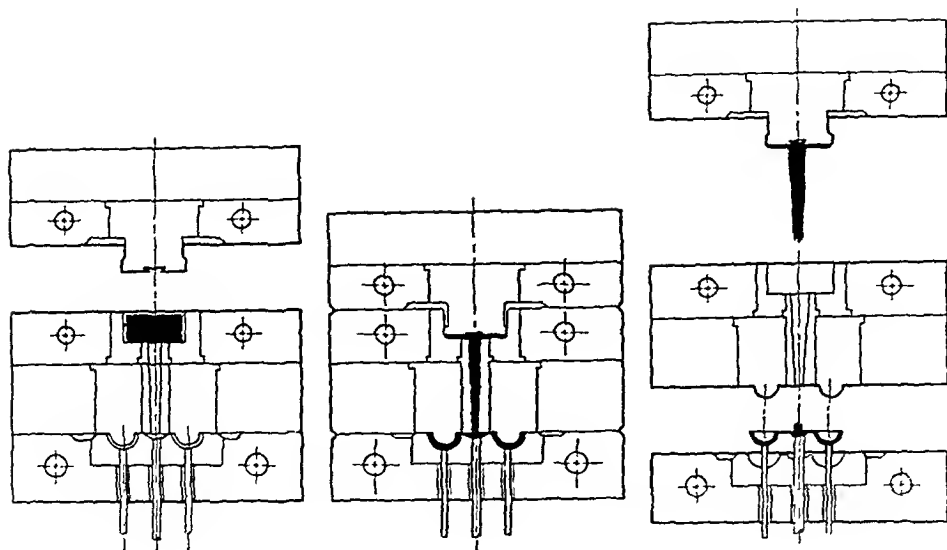


FIGURE 12-35

Typical transfer-mold operation. Material is fed into the pot of the transfer mold and then forced under pressure when hot through an orifice and into a closed mold. After the polymer has formed, the part is lifted by ejector pins. The sprue remains with the cull in the pot [37].

reaction. When the mold is disassembled, note that the part is pushed out of the mold by *ejector pins* that operate automatically. The *sprue* is withdrawn, because of a slight undercut section, along with the *cull*, the uninjected remainder. The *gate* is the point where the sprue meets the *runners* that carry resin from the sprue bushing to the individual cavities.

Because compression molding of a thermoplastic resin involves heating and then cooling the mold, most such materials are more efficiently molded in the injection machines described next. One exception is the production of high-quality phonograph records, usually of compounded poly(vinyl chloride). The thin section, coupled with preheating of resin "biscuits," allows a relatively fast heating, forming, cooling cycle.

Preformed biscuits may be heated to $150 \pm 5^\circ\text{C}$ on a steam table adjacent to the molding machine. The molding press is a flash mold that resembles a waffle iron. The faces of the mold are nickel negatives of an original disc recording that have been made by electrodeposition. At 150 to 170°C and 1800 to 2000 psi (12 to 14 MPa), the record is formed and cooled with a total cycle time of only 40 s. Less expensive records such as children's 7-in discs may be injection-molded from polystyrene.

Injection molding accomplishes the cyclic operation by carrying out each step in a separate zone of the same apparatus. A plunger (also called ram or piston) pushes pellets, which fall from the hopper into the barrel when the plunger is withdrawn (Fig. 12-36) into a heated zone. By spreading the polymer around a *torpedo* into a thin film, rapid heating is possible. The already molten polymer displaced by this new material is pushed forward through the *nozzle*, the sprue bushing, past the gate, down the runner, and into a cooled cavity. The thermoplastic must be cooled under pressure below T_m or T_g before the mold is opened and the part is ejected. The plunger is withdrawn, new pellets drop down, the mold is clamped shut, and the entire cycle is repeated. Mold pressures of 8000 to $40,000$ psi (55 to 275 MPa) and

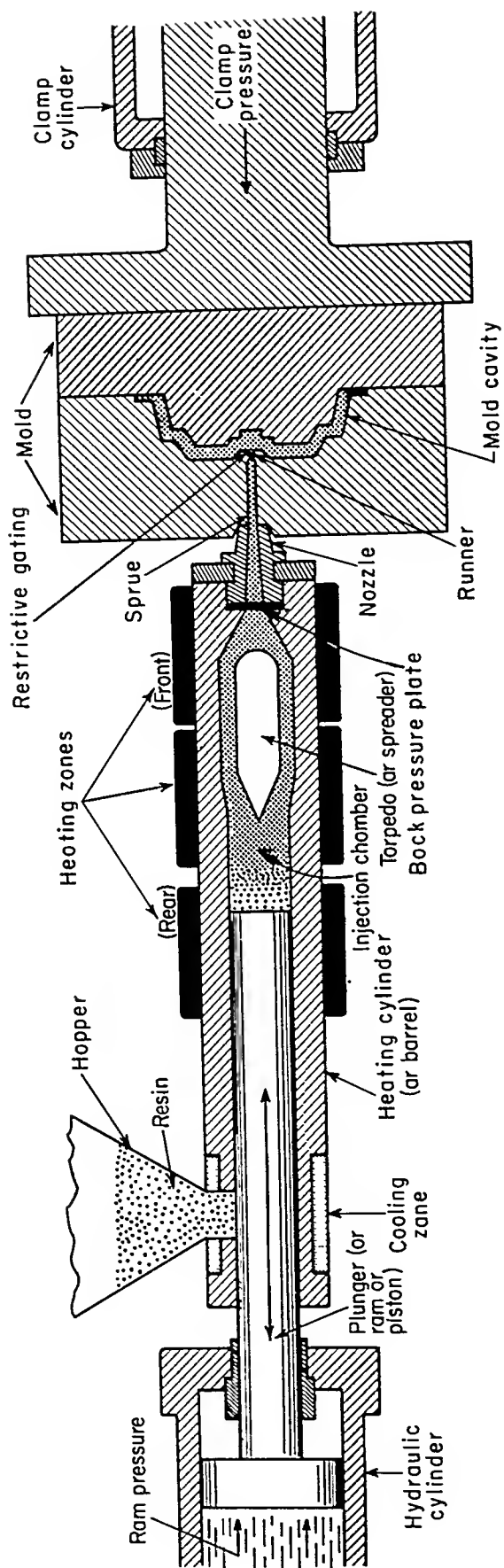


FIGURE 12-36
Schematic cross section of typical plunger (or ram or piston) injection molding machine [18].

cycles as low as 15 s are achieved on some machines. Injection molding machines are rated by their capacity to mold polystyrene in a single shot. A 2-oz machine can heat and push 2 oz of general-purpose polystyrene into a mold. Plunger diameter, plunger travel, and heating capacity all are involved. Although the plunger-type machines are inherently simple, the limited heating rate has caused a decline in popularity, so that most machines being sold today in the United States are of the reciprocating-screw type. By virtue of a check valve on the forward end of the screw (Fig. 12-37), it can push forward without rotation and act just as the plunger in an ordinary injection molding machine. The screw may remain forward while the melt cools or, in the case of rubber, the polymer in a hot mold cross-links. The screw then turns and threads its way back to the rear of the barrel. The check valve is open during rotation allowing molten polymer to flow around the screw. It is in this part of the cycle that the screw is valuable because it increases heat transfer at the walls and also does considerable heating by the conversion of mechanical energy into heat in an adiabatic system. When the finished part is ejected from the mold, the entire cycle can be repeated. Another advantage of the screw machine is its mixing and homogenizing action. Another way of taking advantage of the screw feature is by *preplasticizing* the melt with a screw arrangement which then feeds to a barrel from which the molten polymer can be injected by a ram (Fig. 12-38).

As with extrusion, injection molding of thermoset resins is difficult but possible. In effect a kind of automated transfer molding is used. Injection molding of rubber (with a heated mold and ejection of hot parts) gives faster cycles and pieces with less porosity than flash compression molding. A side benefit is that rubber molded and cross-linked at a high pressure has built in residual stresses that increase resilience. A cross-linked polybutadiene rubber ball will bounce back up to about 85% of its original height when molded at pressures of less than 1000 psi (7 MPa). However, molding at about 10 times that pressure can increase the bounce to as much as 92%. Since this particular property is not of great importance except to toy manufacturers,

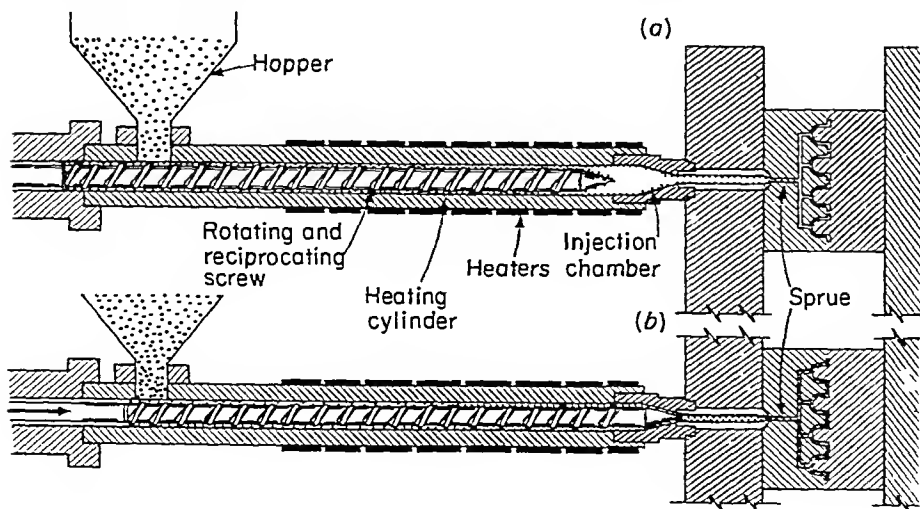


FIGURE 12-37

Cross section of a typical screw injection molding machine, showing the screw in the retracted (a) and the forward (b) position [18].

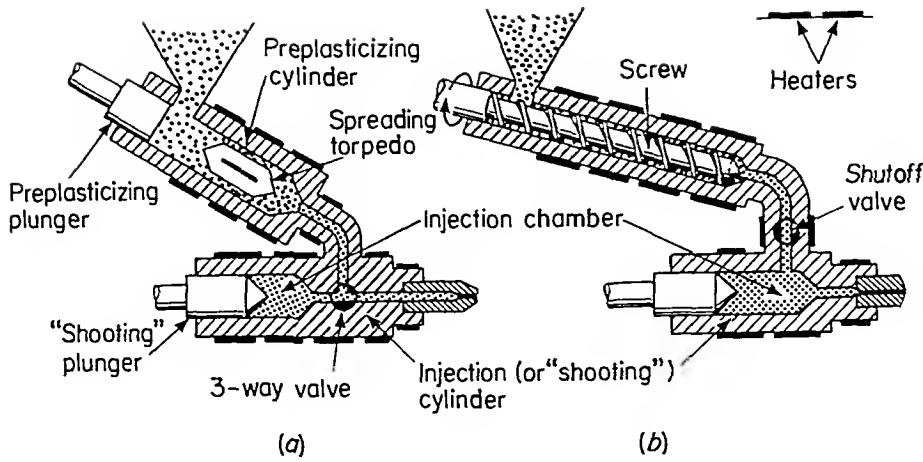


FIGURE 12-38

Drawings of a plunger-type (a) and a screw-type (b) preplasticizer atop plunger-type injection molding machines [18].

the more often cited benefits of injection molding of rubber are the faster cycle time and lower scrap level (less flash, sprues, etc.) compared to compression molding.

The rapidity with which isocyanate-polyol reactions take place has been used to advantage in reaction injection molding (RIM). In the typical process (Fig. 12-39), two components are mixed by high-pressure injection into a special chamber and injected almost immediately into a closed, low-pressure mold. The finished parts can be cellular or solid depending on the amount of material injected and on the formulation used. In the automobile industry, the need for light-weight, cushioning parts has been met by RIM. Front and rear bumpers and the "fascia" (face part, which can include grill and headlight housings) are made as single units.

The mixing head is the critical point in the system. Volume in the mixing chamber is kept small (1 to 5 cm³) and impingement pressures for mixing are 100 to 200 atm. There is a self-cleaning feature so that when one mold is filled, the head will remain clear until another mold is ready. Mold filling may take 2 or 3 s at mold pressures of only 3 or 4 atm. Typical conditions are summarized in Table 12-7. A single metering pump may feed up to 12 mixing heads. In another modification

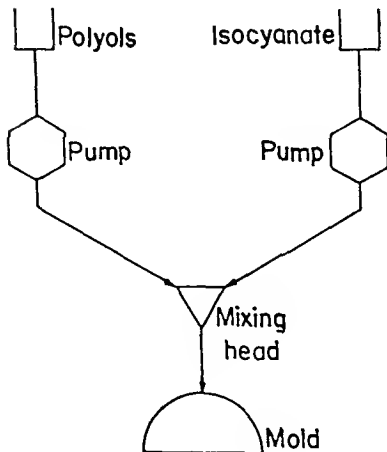


FIGURE 12-39

Reaction injection molding. Polyols and isocyanates are pumped at high pressure from storage reservoirs into the mixing head. The mixed streams are then injected into the mold at a much lower pressure.

TABLE 12-7
Typical Conditions for Reaction Injection Molding [38]

Formulation	Parts by weight
Resin stream:	
Polyols	150
Dibutyltindilaurate (catalyst)	0.045
Amine cocatalyst	0.6
Isocyanate stream:	
Polyfunctional isocyanate	96
Blowing agent (Freon type)	3
Methylene chloride	1
Processing parameter	Condition
Resin temperature	54°C
Isocyanate temperature	21°C
Mold temperature	57 ± 3°C
Resin pressure	120 atm
Isocyanate pressure	100 atm
Throughput	1.1 kg/s
Demolding time	1 to 2 min
Post-cure	1 h at 120°C
Physical property	Value
Density	0.99 g/cm ³
Hardness, Shore D	51
Tensile strength	18.6 MPa (2.7 × 10 ³ psi)
Elongation at break	175%
Flexural modulus at	
−29°C	830 MPa (120 × 10 ³ psi)
+21°C	150 MPa (22 × 10 ³ psi)
+65°C	70 MPa (10 × 10 ³ psi)

called liquid injection molding (LIM), the entire shot for a mold is mixed in a chamber before injection so that it resembles transfer molding.

Rigid structural foams with densities about 0.5 g/cm³ have been used for furniture and for housings for electronic equipment. Low-modulus elastomers such as the material described in Table 12-7 have been used for bumpers. With two mixing machines and eight molds, a production rate can be maintained of 1400 6-kg bumpers per day. Each cycle involves a 3-s injection time and a 2-min demolding time [39]. The addition of milled glass or mineral fillers to RIM formulations has led to high-modulus materials that may find use as automobile fenders [40].

Molding with little or no pressure is practical if the melt viscosity is very low so that the polymer can be *cast* (poured) into a mold and allowed to set by reaction or cooling. Most polymers with molecular weights low enough to be pourable have poor physical strength. Paraffin wax is a good example of a kind of polyethylene with low enough melt viscosity to be poured into a mold. When a cotton string insert is included, such a casting operation produces a candle. Since mold casting of candles goes back at least to colonial times, it ranks as one of the more antique fabricating

methods still in use. Casting a monomer in a mold to make a sheet of acrylic plastic was described in Sec. 5-2. Some other polymers that are cast are the epoxies and the silicones. A highly filled epoxy resin with good cured strength and abrasion resistance can be cast inexpensively to make a metal stamping die. One takes a pattern (same dimensions as final piece), places it in a box, and pours in the resin-hardener mixture (usually with a filler), which sets to a network polymer on heating (Fig. 12-40). After a mold release compound is sprayed on the surface, another layer is poured and set. The two pourings are attached to opposite plateaus of a stamping press and form a matched mold for the forming of metal sheets. Compression and injection molds can be made in the same manner.

Plastisols represent a special heat-convertible liquid category that is made possible by the unique properties of poly(vinyl chloride). The polymer is quite insoluble in a large class of high-boiling liquids including di-2-ethylhexylphthalate. It is possible to disperse finely divided polymer particles in this liquid and have a stable, free-flowing suspension (a *plastisol*) at a weight ratio of 3:5 or higher, liquid to polymer. The polymer particles preferably have been recovered from an emulsion polymerization to aid in the plastisol formation. Such polymers are sometimes called plastisol, dispersion, paste, or stir-in resins. When the plastisol is heated to about 175°C (the temperature varies with resin and plasticizer), the resin rapidly dissolves in the plasticizer. Only a small amount of plasticizer is volatilized at this temperature. On cooling, the solution of resin in plasticizer remains stable indefinitely. It will be recalled that the major effect of a plasticizer is to change the T_g of a system. Examples were given in Sec. 3-6. The utility of such a liquid, castable, heat-convertible system is obvious. Although other polymers have been proposed as plastisol resins, only polymers and copolymers of vinyl chloride seem to have the combination of low-temperature insolubility, high-temperature solubility, and high tensile strength when plasticized

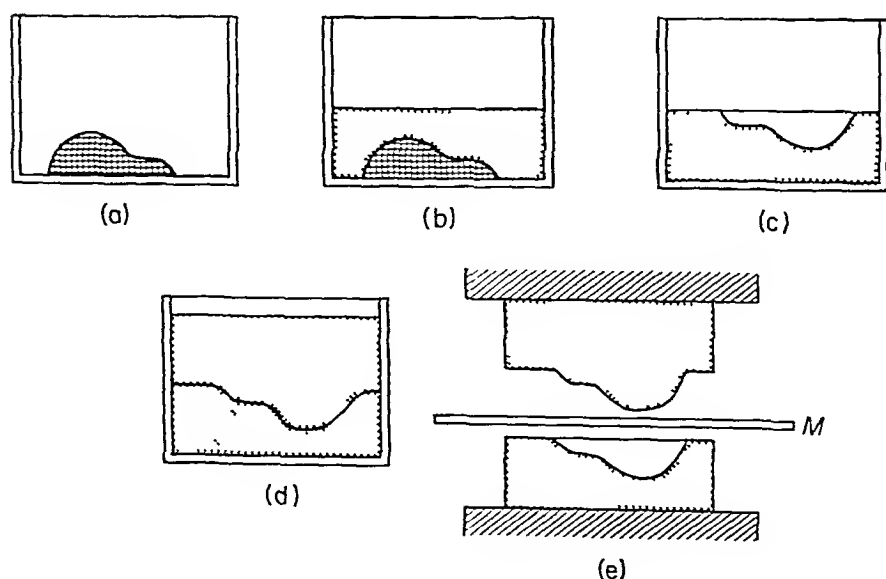


FIGURE 12-40

Making a stamping die from a filled epoxy resin. (a) Pattern placed in box; (b) resin added and hardened to make lower half of die; (c) pattern removed, lower half of die inverted and coated with release agent; (d) resin added and hardened to make upper half of die; and (e) two halves of die mounted in press to form metal sheet, M .

that is needed [41, 42]. While hundreds of liquids are sold as plasticizers, esters of phthalic and adipic acid, along with epoxidized drying oils, chlorinated waxes, and esters of phosphoric acid, dominate the market. Primary consideration may be given to the final properties of the system such as T_g , modulus, strength, stability, and odor. On the other hand, the viscosity of the plastisol initially and on aging often becomes a controlling factor in plasticizer selection. The problems of physical and chemical stability (plasticizer migration and thermal breakdown) are discussed in Chap. 11.

In the laboratory the resin can be dispersed in the liquid by stirring in a beaker with a spatula. Industrially a dough mixer adapted from the baking industry may be used. The unmodified plastisol may have a viscosity of 1 to 100 P (0.1 to 10 Pa·s). To get the best dispersion the mixture may be refined on a three-roll mill or some other high-shear device. Because of the rather high viscosity and surfactant present, air bubbles are trapped. An arrangement for cyclic deaeration of plastisols is shown in Fig. 12-41. Liquid is pulled from the supply tank over a spreading cone to facilitate escape of bubbles. Some compounds, silicone oils, for example, may be added to aid the process. After a short period the deaerated batch can be expelled by compressed air into a receiver from which it is dispensed to casting, dipping, or other operations.

Some articles, such as fishing lures, washers, and stoppers, are made by casting in open molds. A sizable application involves *slush molding*. A typical product made by this technique is an overshoe. There is a great resemblance to fluidized-bed casting (Sec. 12-4). A preheated, hollow metal mold is filled with plastisol and then inverted (Fig. 12-42). The hot wall solvates some resin so that on inversion of the mold the core flows out but the skin remains. Further heating completes the fusion process. Some cooling is necessary before the boot can be stripped from the mold. The mold might be split to facilitate removal of the molded object, which now bears on its

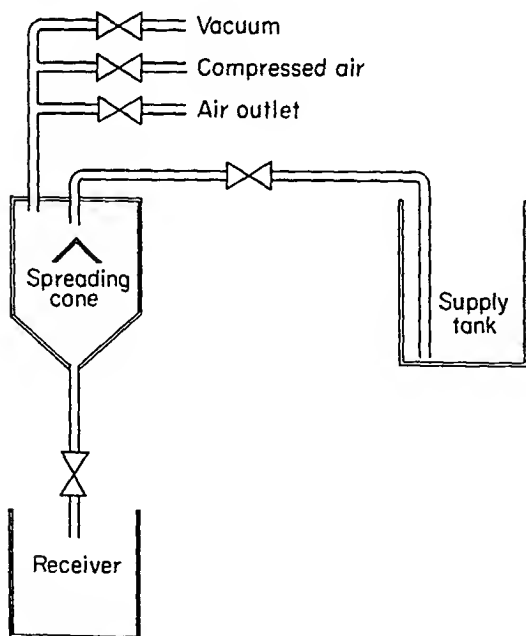


FIGURE 12-41

Schematic diagram of a deaeration device for plasticizer-poly(vinyl chloride) dispersions [41].

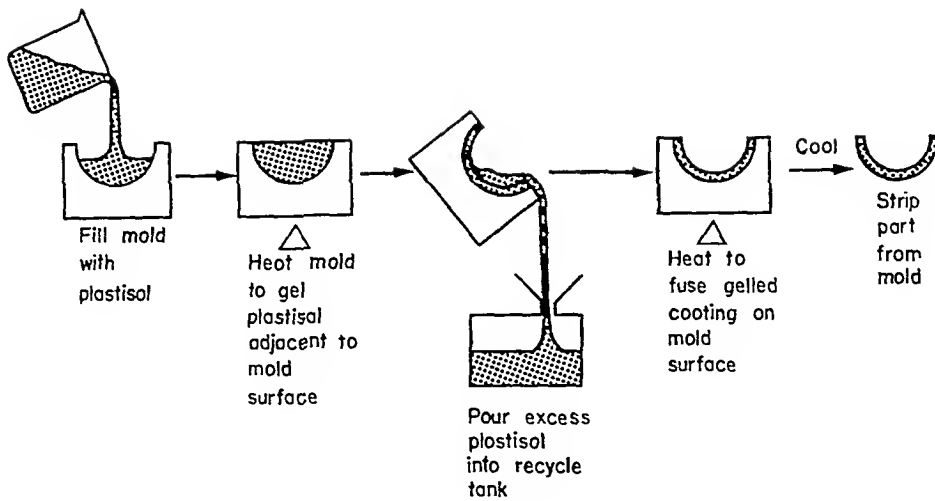


FIGURE 12-42
Slush molding process. (Courtesy of Union Carbide Corp.)

outer side the pattern from the inner side of the metal mold. Squeezable dolls or parts of dolls are most often made by slush molding.

Even closer to the fluidized-bed technique is the process of *dipping* (Fig. 12-43). Wire dish drainers, coat hangers, and other industrial and household metal items can be coated with a thick layer of flexible vinyl plastic by simple dipping and fusion. A more elaborate artifact is a plastic glove, which could be produced either by dipping a hand-shaped mandrel or by slush molding in a hollow mold of the same shape. Several variations of the plastisol have been developed to alter the properties of the liquid as well as the final solid.

The viscosity of the plastisol increases as the ratio of resin to plasticizer in-

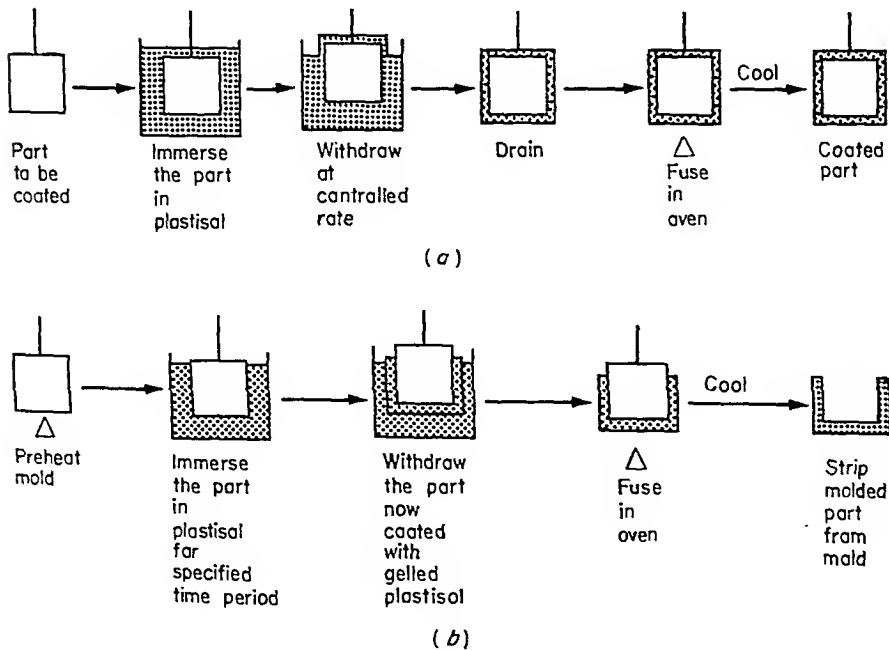
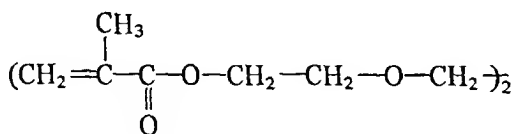


FIGURE 12-43
Plastisol dipping. (Courtesy of Union Carbide Corp.)

creases. Where a thin coating of a rigid product is required and the plasticizer content is so low that the plastisol will not flow easily, a nonsolvating diluent can be added. The process of solidification is more complex now, since the diluent (usually an aliphatic or naphthenic liquid in the mineral spirits range) must evaporate before the fusion is attempted. *Organosols*, as these diluted plastisols are termed, are used to advantage in dipping processes as well as in impregnating cloth or rope with vinyl polymer. There are some applications where it is desirable to have an infinite viscosity at low shear stresses. *Plastigels* are made by adding to the resin-plasticizer suspension a metallic soap or finely divided filler as a gelling agent. Aluminum stearate is an effective gelling agent, especially if a petroleum oil is being used as a secondary (extending) plasticizer. The suspension of resin in gelled plasticizer can be cold-molded, placed on a pan, and heated to fusion without discernible flow. The whole operation resembles baking cookies, with molding and baking being done in two separate steps.

There are two routes to making fluid plastisols that become rigid when fused. One is to extend the easily dispersed emulsion process resin with a larger-particle-size, dense, suspension-process resin. The latter may be 10 to 50 μm in diameter compared with the ultimate particles of the former, which are in the 0.1- to 1- μm -diameter range. The larger particles remain suspended because of the thickening action of the small ones. A slightly longer fusion time may be required to get complete solvation. Very rigid, glassy solutions can be made when the plasticizer can be polymerized during or right after fusion. For example, a *rigidsol* might be made from 100 parts of poly(vinyl chloride) and 100 of triethylene glycol dimethacrylate, together with one part of di-*tert*-butyl peroxide. The viscosity of the mixture is only 3 P compared to 25 P for a phthalate-plasticized material. However, on fusion for 10 min at 175°C, the resin solvates and the plasticizer forms a network almost simultaneously. Back at room temperature, the baked product is a hard, rigid glass with a flexural modulus of over 2.5×10^5 psi (1.7 GPa).



Triethylene glycol dimethacrylate

Slush molding has been mentioned as one method of producing a hollow object. Several others have been developed. *Rotational* molding can be used with plastisols, but it can be also be used with finely divided powders of polyethylene and other polymers (Fig. 12-44). In this case the hollow, split mold is charged only with enough material to make the final object. The mold is closed and heated while being rotated in an eccentric manner so that all surfaces on the inside of the mold become coated with a fused material. Cooling, opening the mold, and removing the hollow object go rather rapidly, since heat transfer is to a thin skin through a metal wall. Large containers, suitcases, and display novelties are inexpensively produced from a lightweight mold that undergoes no great stress during the process.

The need for a rapid production of bottles with uniform thickness for bleaches, milk, and a myriad of other household products is best met by *blow molding*. A tube

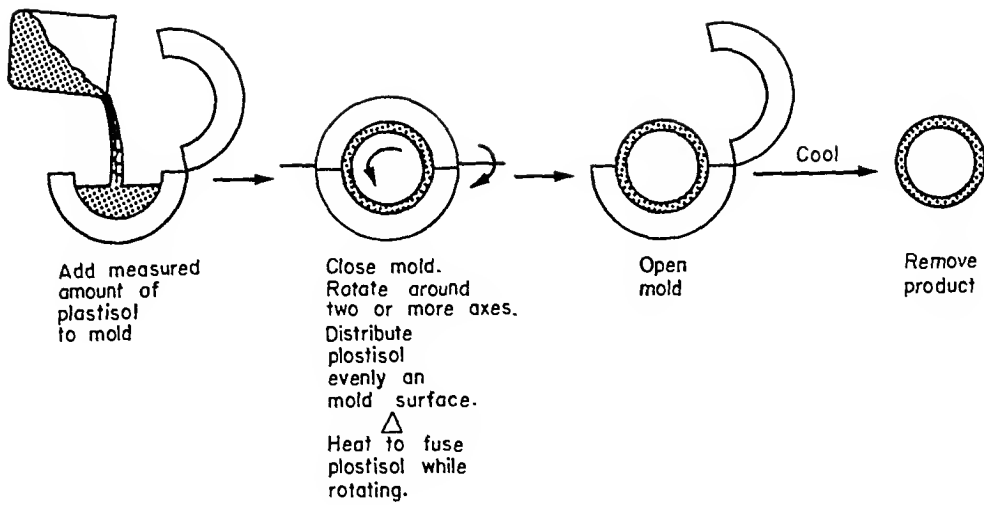


FIGURE 12-44

Rotational molding process. (Courtesy of Union Carbide Corp.)

of molten polymer, the *parison*, is sealed at both ends and held in place while two halves of a hollow mold surround it. Air is injected into the parison, which blows up as if it were a rubber balloon. When the polymer surface meets the cold metal wall of the mold, it is cooled rapidly below T_g or T_m . Once the product is dimensionally stable, the mold is opened, the bottle is ejected, a new parison is introduced, the mold is closed, and so on. The parison can be produced continuously from a screw extruder and converted to a bottle on a rotating platform (Fig. 12-45). In the ram-extrusion method, the parison is formed in a cyclic manner by a plunger forcing a charge out from an accumulated molten mass as in the preplasticizer injection-molding machine (Fig. 12-46). In the production of large bottles, efficiency demands a rather uniform wall thickness and no dangerous thin spots. Inherently the weight of the bottom of a parison that is suspended vertically from a machine will cause the wall to be thinner

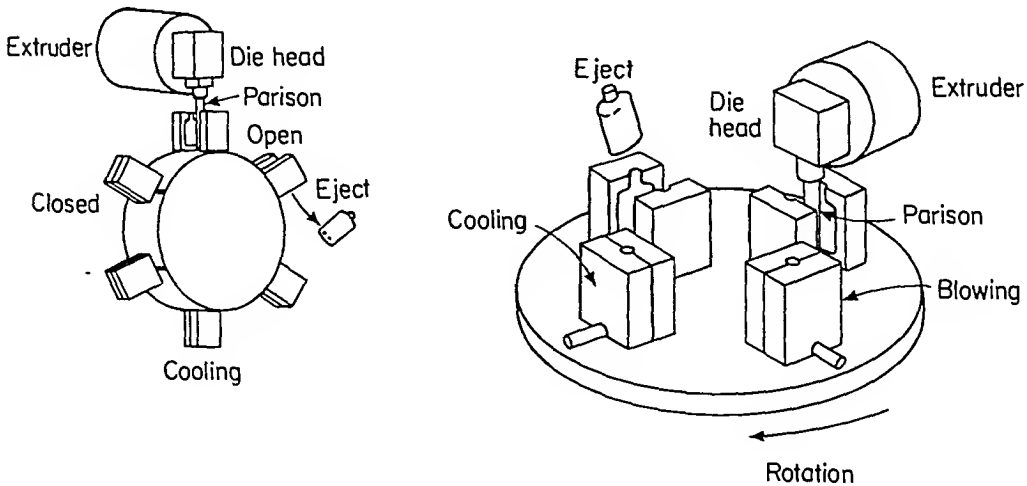
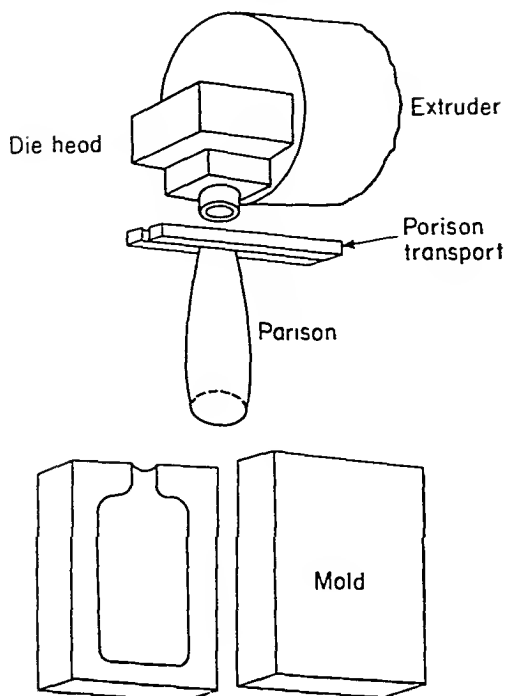


FIGURE 12-45

Vertical wheel type of continuous extrusion blow molding machine; molds are carried to the die head by rotation of the wheel. In a horizontal table type all steps of the process are carried out simultaneously also [43].

**FIGURE 12-46**

In this continuous extrusion, blow-molding system, a parison transfer device is used to lower the extruded parison from the die head into the waiting mold. The transport arm cuts and holds the parison during the transfer operation [43].

toward the top. Unless corrected, a long parison may give a bottle with a wall thickness near the bottom twice that near the top. One way to correct the situation is to program the position of a mandrel around which the parison is being extruded so that the die opening increases during a shot (Fig. 12-47). The parison now has a thicker wall toward the top, which will be evened out as it hangs waiting a second or two to be molded. Cycles are fast. Small plastic vials can be molded 10 at a time from one machine with multiple cavities using a cycle time of 10 s.

In *stretch-blow* molding, biaxial orientation in the bottle is increased by longitudinal stretching during radial blowing. This is accomplished by an internal rod (Fig. 12-48). Better clarity, increased impact strength, and improved barrier properties (water and gas diffusion) are claimed. Beverage bottles made from poly(ethylene terephthalate) have used the technique.

Large moldings of glass fiber-reinforced polyester often are made using low pressures. A number of variations exist. A typical resin formulation might contain 30 to 40% styrene monomer with the balance being an unsaturated polyester (based on maleic anhydride, for example). The glass reinforcement can be in chopped strands, mats of strands, woven cloth, or continuous filaments.

For the production of a boat hull or an automobile body, layers of glass cloth or mat can be placed on a form and then impregnated by pouring "activated" resin from a pail. The activation usually consists of a peroxide initiator with an accelerator like cobalt naphthenate. The resin is spread out with rollers and polymerization

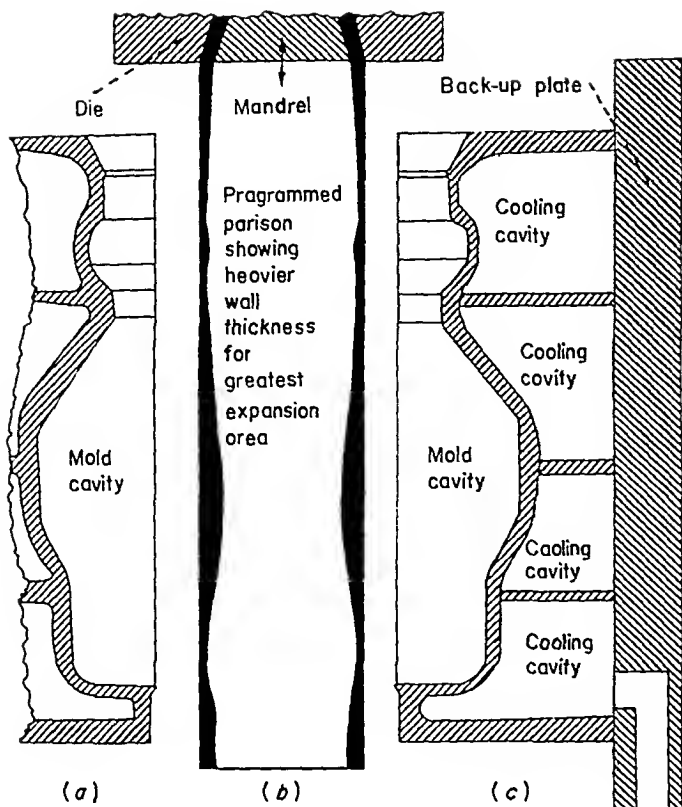


FIGURE 12-47

A programmed parison designed to fit a particular mold configuration [44].

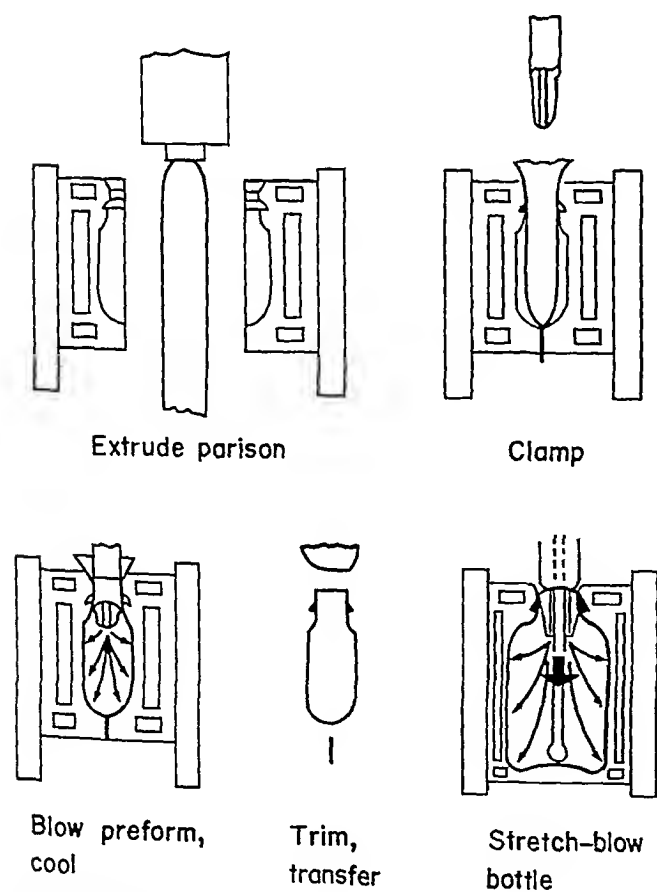


FIGURE 12-48

Stretch-blow molding [45].

takes place after an induction period ("pot life") of an hour or so at room temperature. If production volume justifies the added cost, a matched-metal compression mold can be used to give a denser, stronger finished product. The hand layup may still be used. A more uniform product is obtained if the glass fibers are sprayed onto the form or if resin and glass are sprayed on simultaneously.

Another means of enhancing uniformity is to combine glass and resin beforehand. Sheet molding compound (SMC) is one approach [46]. When the liquid polyester (actually polyester plus styrene) is thickened by less than 1% of calcium or magnesium oxide, the gel has a yield stress and can be handled without dripping. SMC is made by combining thickened polyester, fillers, peroxides, and chopped glass fiber between layers of polyethylene. The mat can be produced continuously and uniformly. Molding requires stripping off the polyethylene film. The amount of SMC can be tailored to the requirements of the piece being molded. It is usually molded under some pressure and with heating.

Bulk molding compound (BMC) is a putty-like mixture of polyester and chopped fiber glass strands [47]. Fillers like calcium carbonate are the factor that changes the liquid polyester to a putty that can be applied with a trowel.

Foams

Foamed polymeric materials have several inherent features that combine to make them economically important. Any foamed material is a good heat insulator by virtue of the low conductivity of the gas, usually air, contained in the system. A glassy polymer when foamed will have a much higher ratio of flexural modulus to density than when unfoamed. A beam of foam deflects less than an unfoamed beam of the same length, width, and weight under the same load. Finally, any foam will have energy-storing or -dissipating capacity operating through a greater distance than the unfoamed material. The resilient foam made when the polymer is rubbery can store most of the energy reversibly and makes a good cushion for upholstery and packaging applications. A compressible foam that breaks down on impact can absorb a great deal of energy and is widely used for packaging. The mere bulk of highly foamed polymers along with good machinability, makes them economical for some decorative purposes where massiveness, without great weight, is demanded. One example is foamed polystyrene used as an artistic medium. A block of foam can be sculptured much as the artist might use clay for three-dimensional figures.

Foams can be classified according to several schemes. The nature of the cells is one. Each cell may be completely enclosed by a membrane or it may be interconnected with its neighbors. *Closed-cell* foams typically are produced in processes where some pressure is maintained during the cell-formation process. *Open-cell* foams often are made during a free expansion. Most processes produce both kinds. In some applications there is an advantage to converting all cells to the open variety. A closed cell tends to store energy reversibly as if it were a small rubber balloon. In cushioning applications it is desirable to have compression cause the flow of air from cell to cell as if they were a series of orifices. This dissipates energy that is not entirely regained on unloading. An open-cell foam acts as a sponge, soaking up liquid by capillary action. A closed-cell foam makes a better buoy or life jacket because the cells do not fill with liquid.

Foams differ in the process conditions under which they are generated. A material that requires a high temperature or an external pressure for foam formation cannot be easily *foamed in place*, as could a system that can be mixed and poured at room temperature. And, of course, the polymer from which the foam is derived can be a thermoplastic or a thermoset, rubbery or glassy.

Foamed polyurethanes, rubber, and poly(vinyl chloride) dominate the upholstery market, so it is convenient to consider the rather different processes that are used for each. Our earlier consideration of polyurethane foams (Sec. 4-5) showed only diisocyanate, water, and polyhydroxy compound as the ingredients. An actual foam formulation is more complex (Table 12-8). A combination of a diol and a triol is used to give a partially cross-linked structure in the final form. The diisocyanate is a mixture of two isomers that differ slightly in reaction rate. The mixture is less expensive than either pure compound. The isocyanate group reacts slowly with the secondary hydroxyl groups that these polymers have on one end. The tin compound catalyzes the reaction, especially in the presence of a small amount of tertiary amine. Note that the amine has no reactive hydrogen. The silicone surfactant is an essential ingredient that regulates the cell size, uniformity, and nature to a large extent, controlling the viscosity and surface tension of the cell membranes as they are stretched during foaming. The last ingredient is a low-boiling liquid (bp 23.8°C) that volatilizes when the urethane reaction starts. The "blowing agent," as this fluorinated hydrocarbon is termed, increases the total volume as indicated without itself participating in the chemical reactions that are occurring. Concern for environmental air pollution by fluorocarbon vapors is an incentive to replace this particular ingredient with other volatile liquids.

The foaming reaction takes place so rapidly that large-scale production demands automatic mixing equipment. In one arrangement, mixing and reaction start in a traveling head that cycles back and forth to make a continuous slab (Fig. 12-49).

The urethane foam is a typical polymer system in that the number of variables that can significantly affect important properties is very large. The optimization of the

TABLE 12-8
Urethane One-Shot Foam System [48]

Ingredient	Parts by weight
Poly(propylene oxide) $M_n = 2000$, 2 OH/molecule	35.5
Poly(propylene oxide) started on tri- functional alcohol, $M_n = 3000$, 3 OH/molecule	35.5
Toluene diisocyanate (80% 2,4- and 20% 2,6-substituted)	26.0
Dibutyl tin dilaurate	0.3
Triethyl amine	0.05
Water	1.85
Surfactant (silicone)	0.60
Trichloromonofluoromethane, CCl_3F	12
Final density = 1.4 lb/ft ³ (2.0 lb/ft ³ if CCl_3F omitted).	

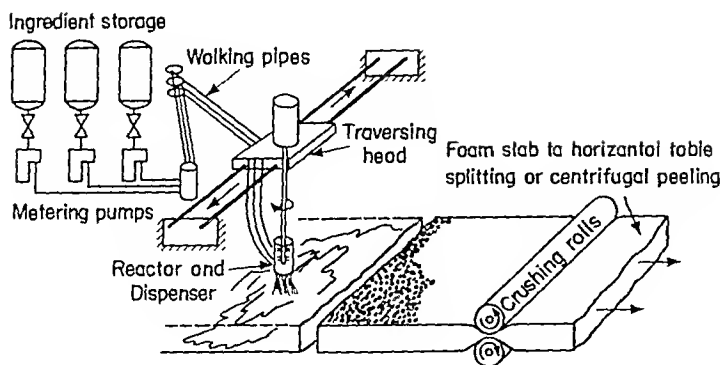
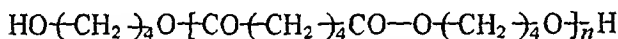


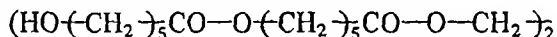
FIGURE 12-49

Continuous urethane foam slab production [49].

relative quantities of only the specific ingredients in Table 12-8 is in itself a time-consuming, expensive exercise even with the aid of a computer and multiple-regression analysis. We must add to that problem the possibilities of varying each ingredient chemically. The polyol can vary in functionality with as many as five or six hydroxyls per molecule. Although polyols based on propylene oxide dominate the field, other polyethers are used based on tetrahydrofuran, ethylene oxide, or styrene oxide. Polyesters are widely used in rigid foams and, to a certain extent, in flexible foams. Such polyesters may be made with an excess of diol or by growth of a hydroxy acid on a

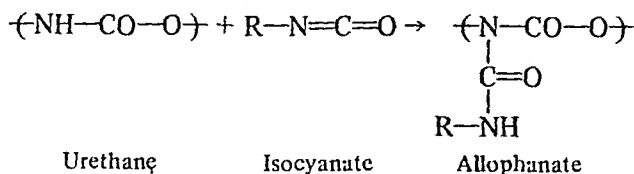


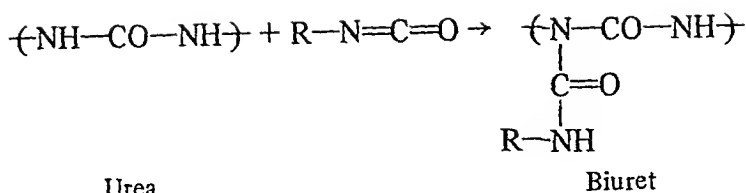
Polyester diol based on butanediol and adipic acid



Polyester diol based on caprolactone "grown" on ethylene glycol

diol. The diisocyanate most often used in foams is the toluene derivative, but the ratio of isomers can be changed. The remaining ingredients present similar opportunities for exploration. Even a single company may offer a line of a half dozen to a dozen surfactants, catalysts, blowing agents, or auxiliary materials. Water is not an essential ingredient. Some urethane foams are made with only the blowing agent. Another parameter that affects foam properties is the manner in which mixing takes place and the time scale of the process. All these things not only can change the physical appearance of the foam, cell size, size distribution, openness, and strength but also can encourage or diminish subsidiary chemical reactions depending on the concentration of reactants, the temperature, and viscosity of the system. Some groups that form in a typical foam, in addition to urethane and urea which were mentioned before, are the allophanate and biuret. It is seen that these represent secondary reactions of the





previously formed groups that still contain an available hydrogen. However, the hydrogen is not as easily reacted as the hydrogen of an alcohol or primary amine. The groups occur less frequently than the urethane and urea and can probably be dissociated more readily under conditions of higher temperature or hydrolytic attack. Nonetheless, they are covalent cross-links and make a definite contribution to modulus and permanent set.

Rigid foams result when the polyol is short-chained and highly functional so that the distance between cross-links is small or when the polyol backbone contains bulky groups that raise the glass-transition temperature. Fillers such as fibers or finely divided silica can be used to stiffen a foam, but they are seldom used because they increase the density of the system. Polyisocyanates of high functionality can be employed to increase the cross-link density. Some of these are condensation products of the commonly used toluene diisocyanate.

One of the largest markets for flexible urethane foams is in upholstery. Danish Modern furniture, with its straight lines and flat cushions, is a large-scale consumer product eminently suited for using polyurethane foam. The foam is made in continuous loaves several feet in width and height and then sliced into slabs of the required thickness. Some other products are crash pads for automobiles and packaging. Weather stripping is made from a thin tape of foam about 6 mm X 3 mm that is attached to a door frame by means of paper tape that has adhesive on both surfaces. Rigid urethane foam can be foamed in place. One of the early commercial applications (1940s) was the filling of certain aircraft components with rigid foam. The advantages of the urethane foam are that it can be foamed in place, say in the rudder or aileron, it adheres well to metal surfaces (as a rule), it adds little weight, and it greatly reduces the flexing of the element on stressing. Hollow walls in chambers such as boxcars can be filled with foam to provide strength and good thermal insulation. Completely open-cell foams can be produced directly in the foaming process by chemical or mechanical treatment of a previously formed material. These "reticulated" foams are widely used as air filters.

Although foamed rubber has many of the same properties as foamed urethanes, the foaming and the cross-linking of the polymer are accomplished in a radically different manner. A simplified outline of the process is shown in Fig. 12-50. To natural rubber latex is added a solution of a soap that yields a froth on beating. In addition, antioxidants, cross-linking agents, and a foam stabilizer are added as aqueous dispersions. Foaming can be done with an eggbeater type of wire whip, but most processes today use automatic mixing and foaming machines that combine agitation and aeration. The foam would collapse rapidly if it were not for the stabilizer, which usually is sodium silicofluoride, Na_2SiF_6 . The hydrolysis of this salt yields a silica gel that increases the viscosity of (gels) the aqueous phase and prevents the foam from collapsing. The cross-linking agent has to act at 100°C or lower *in order to react before*

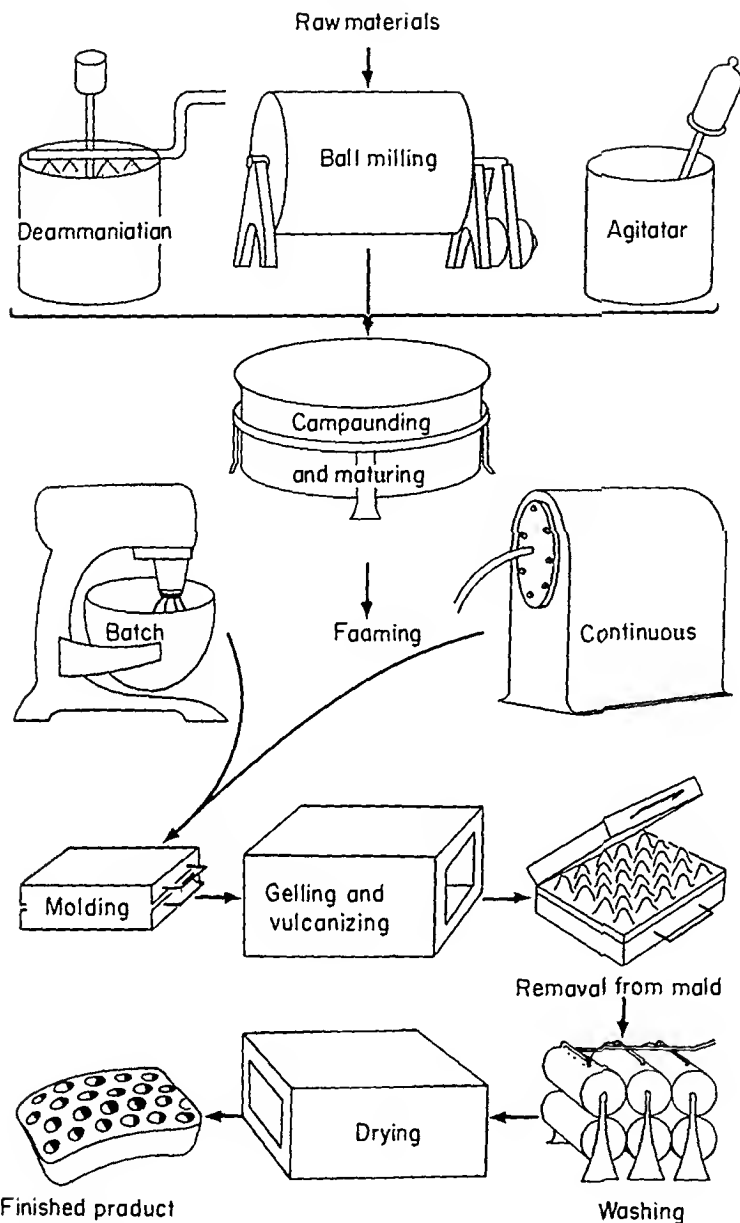
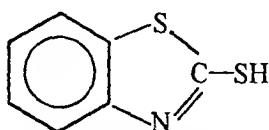


FIGURE 12-50
Sequence of operations in latex foam manufacture [50].

the water is removed from the foam. One such combination is sulfur with the zinc salt of mercaptobenzothiazole:



Mercaptobenzothiazole

Cross-linking (curing or vulcanization) takes place in 30 min at 100°C. In a large article such as a mattress, a metal mold is filled with the foam during the few minutes between the time foaming is complete and the silica gel has formed. The entire mold is then heated by steam at atmospheric pressure. After being removed from the mold, the foam may be dewatered by compression between rolls or centrifuging followed by drying with hot air in a tunnel dryer. Part of the natural latex can be replaced by a synthetic rubber such as the latex from emulsion copolymerization of styrene and butadiene. The overall composition of such a combination in Table 12-9 illustrates again the complexity of simple "model" systems in the real world.

Although poly(vinyl chloride) foams cannot be made as inexpensively as those from rubber or urethanes, their mechanical properties can sometimes be of value. Most vinyl foams are stronger and are torn less easily than rubber or urethane foams of comparable density and are less flammable. Two processes for making foamed poly(vinyl chloride) use *plastisols* (see Sec. 12-6, *Molding*). The first is a very generally applicable method that can be used whenever a system can be mixed at a lower temperature than the decomposition temperature of a *blowing agent*. Three important characteristics of a blowing agent are the decomposition temperature, the volume of gas generated per unit weight, and the nature of the decomposed residue. Several examples (Table 12-10) are especially recommended for vinyl plastisols [52]; in each case the gas generated is nitrogen. Carbon dioxide can be generated by heating some inorganic carbonates. To produce uniform cells the blowing agent must be uniformly dispersed or dissolved, uniformly nucleated, and rapidly, smoothly decomposed over a narrow temperature range, which is matched to the attainment of a high viscosity or gelation of the polymer system. In plastisols, gelation involves the solvation of resin in plasticizer at 150 to 200°C, depending on the particular ingredients employed. If gelation occurs before gas release, large fissures or holes may form. Cells formed too soon before gelation may collapse and give a coarse, weak, spongy material. Closed cells result when the decomposition and gelation are carried out in a closed mold almost filled with plastisol. After the heating cycle, the article is cooled in the mold still under pressure until it is dimensionally stable (about 50°C). It expands slightly

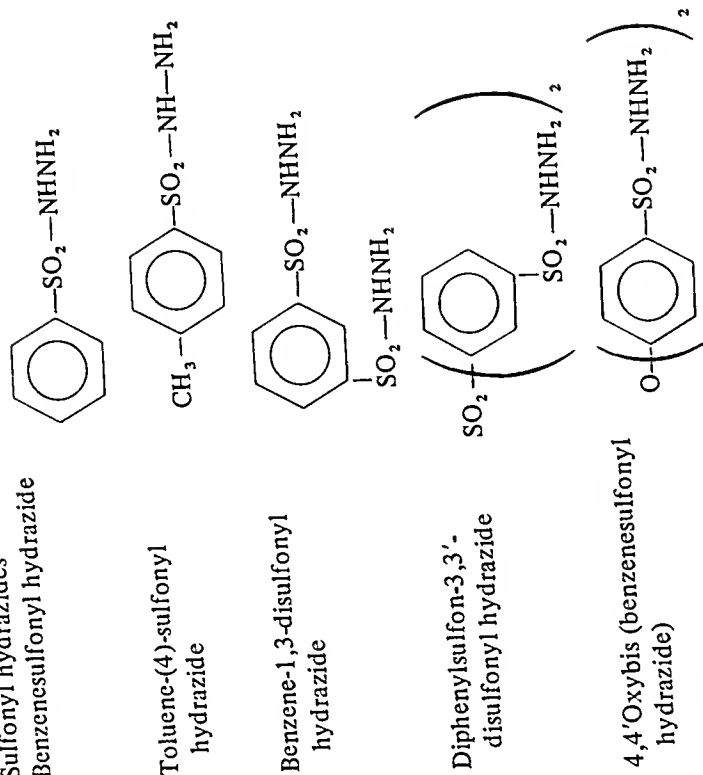
TABLE 12-9
Foamed Rubber Formulation [51]

Ingredient	Parts by weight
Styrene-butadiene latex (65% solids)	123
Potassium oleate	0.75
Natural rubber latex (60% solids)	33
Sulfur	2.25
Accelerators:	
Zinc diethyl dithiocarbamate	0.75
Zinc salt of mercaptobenzothiazole	1.0
Reaction product of ethyl chloride, formaldehyde and ammonia ("Trimene Base")	0.8
Antioxidant (phenolic)	0.75
Zinc oxide	3.0
Na ₂ SiF ₆	2.5

TABLE 12-10
Commercial Foaming (Blowing) Agents [52]

Chemical description	Structure	Decomposition temperature in air, °C	Decomposition range in plastics, °C	Gas yield ml(STP)/g	Literature reference
A. Azo compounds					
Azobisformamide (Azodicarbonamide)	$\text{H}_2\text{N}-\text{CO}-\text{N}=\text{N}-\text{CO}-\text{NH}_2$	195-200	160-200	220	BIOS Final Report 1150, 23 German Patent 871,835
Azobisisobutyronitrile	$\begin{array}{c} \text{CH}_3 \qquad \text{CH}_3 \\ \qquad \quad \\ \text{NC}-\text{C}-\text{N}=\text{N}-\text{C}-\text{CN} \\ \qquad \quad \\ \text{CH}_3 \qquad \text{CH}_3 \end{array}$	115	90-115	130	German Plastics Practice, DeBell-Richardson p. 456 (1946) German Patent 899,414
Diazoaminobenzene		103	95-100	115	U.S. Patent 2,299,593
B. <i>N,N</i> -Nitrosocompounds					
<i>N,N'</i> -Dimethyl- <i>N,N'</i> -dinitrosoterephthalamide	$\begin{array}{c} \text{H}_3\text{C}-\text{N}-\text{OC}-\text{C}_6\text{H}_4-\text{CO}-\text{N}-\text{CH}_3 \\ \qquad \quad \qquad \qquad \qquad \\ \text{NO} \qquad \qquad \qquad \text{NO} \end{array}$	105	90-105	126*	U.S. Patent 2,754,326
<i>N,N'</i> -Dinitrosopentamethylenetetramine	$\begin{array}{c} \text{CH}_2-\text{N}-\text{CH}_2 \\ \qquad \quad \\ \text{ON}-\text{N} \qquad \text{CH}_2-\text{N}-\text{NO} \\ \qquad \quad \\ \text{CH}_3-\text{N}-\text{CH}_3 \end{array}$	195	130-190	265†	U.S. Patent 2,491,709

C. Sulfonyl hydrazides



German Patent 821,423
and U.S. Patent
2,626,933

>95	95-100	130	}
103	100-106	120	
146	115-130	85 [†]	
148	120-130	110	Same as above
150	120-140	125	Same as above and U.S. Patent 2,552,065

*70% active.

†100% active.

‡50% active.

on removal from the mold because of the compressed gas it now contains. Final expansion is accomplished by heating the free article somewhat below the previous molding temperature. Buoys, life jackets, floats, and protective padding are some items made by this process.

The same blowing agents can be used in making foamed rubber. The step corresponding to fusion of plastisols is the cross-linking reaction to give a stable network (vulcanization). Some thermoplastics such as polyethylene and cellulose derivatives can also be foamed by blowing agents even though they do not undergo an increase in dimensional stability at an elevated temperature. As long as the polymer melt is viscous enough to slow down collapse of the cells and the system is cooled below its T_m or T_g , a reasonably uniform cell structure can be built in.

When the plastisol containing a blowing agent is spread on a substrate and fused without a second confining surface, the cell structure is usually open. Fabrics with a bonded layer of insulation are made this way. Extrusion can also be used with a variety of thermoplastic and rubber compounds. Foamed gaskets and weather stripping are made by decomposing the agent in the barrel of the extruder and allowing the extrudate to expand freely. The product is predominantly open-celled.

Plastisols can be used in a mechanical foaming process. A substantial amount of carbon dioxide will dissolve in the plasticizer phase when mixed at about 7 atm and below room temperature. Release of pressure through a nozzle yields a stream of foamed, unfused plastisol. In order to convert this to the stable, fused plasticized vinyl product, two innovations have been introduced. A gelling agent, an aluminum soap, is used to make the liquid plastisol into a highly pseudoplastic fluid, which flows easily at high stresses but is extremely viscous at low stresses. Even with the gelling agent, the cells would collapse on fusing the resin-plasticizer mixture in an oven that depended on slow heating by conduction through the foam, which is an excellent thermal insulator. Dielectric heating can be used to heat uniform cross sections and results in very rapid fusion throughout the foamed mass. The whole process of cooling and dissolving carbon dioxide in the plastisol using a scraped-surface heat exchanger, pressure release through a nozzle, gelation, and fusion can be carried out continuously, since the fusion can be accomplished in seconds by dielectric heating.

The foams based on urethanes, rubber, and vinyls discussed so far are flexible and useful for upholstery and packaging. Increasing the degree of cross-linking will make any one of them more rigid. Of the three, only the urethanes are important in the commercial applications of rigid foams. Another way to achieve rigidity is to use a polymer that is below T_g at normal use temperatures. The various forms of polystyrene foams illustrate techniques that can be applied to other thermoplastic polymers.

A solution of polystyrene in methyl chloride can be heated well above the normal boiling point as long as the system is kept under pressure as in the barrel of an extruder [53]. Upon issuing from the extruder, the solvent evaporates, simultaneously foaming the plastic and cooling it below the T_g . Foaming and dimensional stabilization thus are carried out in one step. Rather extensive facilities are required to mix and convey the concentrated solution and to extrude the foamed "logs." Because it is uneconomical to ship low-density foams a great distance, a modification of the solution process has been introduced [54]. Pellets chopped from an ordinary

melt extruder or beads from a suspension polymerization are impregnated with a hydrocarbon such as pentane. As long as the beads or pellets are stored below 20°C , the vapor pressure of the pentane dissolved in the polymer is low enough that pressures of less than one atmosphere build up in a closed container. Even so, manufacturers do not recommend storing the impregnated material more than a few months. The pellets may be used in an extrusion process to give logs or thin sheets. Usually a nucleating agent is added, such as citric acid or sodium bicarbonate [55], to control the cell size. This process has been especially successful in producing thin sheet that can subsequently be formed into containers. Tubular blow extrusion is used (Fig. 12-51). Egg cartons and cold drink cups can be made by the thermoforming techniques mentioned in the next section starting with foamed sheet.

The beads often are molded in a two-step process. Prefoaming almost to the density that will be required in the final object is similar to corn-popping. Steam heat is used in an agitated drum (Fig. 12-52) with a residence time of a few minutes. The expanded beads can be stored for as much as a few weeks before final molding. In a typical mold (Fig. 12-53) prefoamed beads are loaded into the mold cavity. After the mold is closed, steam is injected. The prefoamed beads expand further and fuse together as the temperature exceeds T_g . The article must be cooled in the mold to a temperature below T_g before removal. Packages shaped to fit their contents, picnic coolers, drinking cups, toys and small sailboats, are common consumer items fabricated from beads. The thin-walled cups demand a small bead for easy flow into the molding cavity. For insulating applications, the variation of thermal conductivity with density and temperature is important (Fig. 12-54).

Foams of phenol-formaldehyde resins can be made from a dispersion of a volatile diluent (isopropyl ether dispersed with the aid of a surfactant) in an aqueous solution of an incomplete phenol-formaldehyde reaction product [58]. Addition of an acid catalyst such as hydrochloric or sulfuric acid causes further condensation

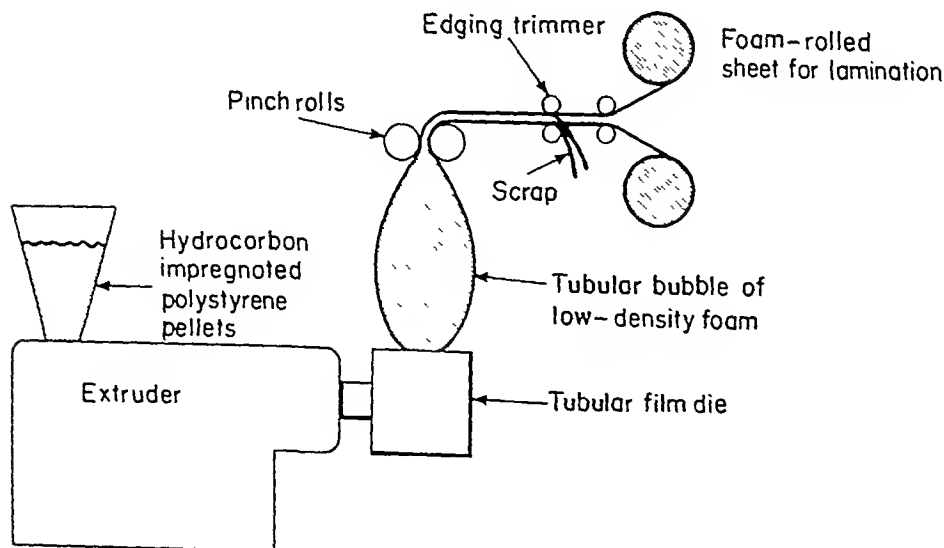


FIGURE 12-51

Production of low-density polystyrene foam sheet from tubular film die [54].

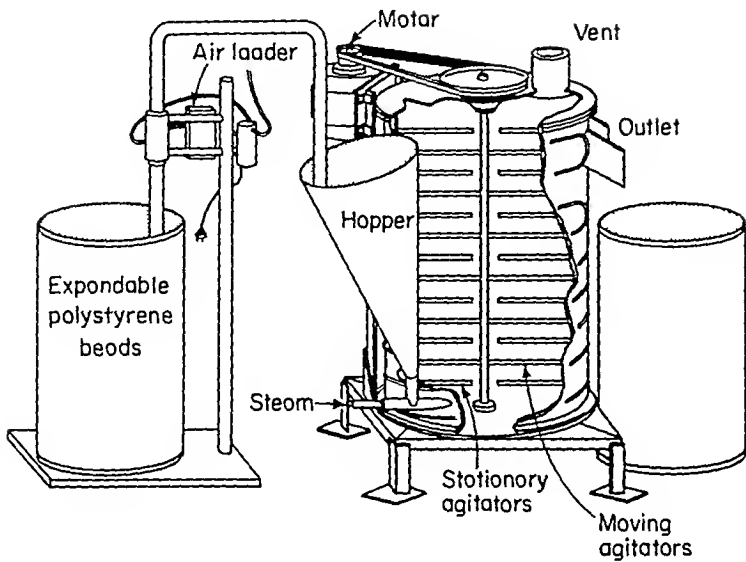


FIGURE 12-52
Prefoaming of polystyrene beads in a steam-heated device [56].

of phenol and formaldehyde to give a dimensionally stable, network structure. At the same time the heat of reaction volatilizes the diluent, yielding a foam. The foaming can be done in place. Phenolic foams are used as heat-stable, flame-retardant, thermal insulation.

Another way to make a foam is to embed hollow spheres of glass or phenolic resin in another polymer. Usually the spheres are mixed with low-viscosity liquids that can be converted to solids. The spheres are not easily dispersed without breaking when extremely viscous rubbers and melts are used.

The structural foam process gets its name from the application for its product rather than the mechanics of the process itself [59]. In a manner directly opposite to the vented extruder (Fig. 12-13), a blowing agent, often nitrogen, is injected into the melt in the extruder (Fig. 12-55). Polymer melt that has already been injected with gas goes to the accumulator. When a sufficient charge has accumulated it is

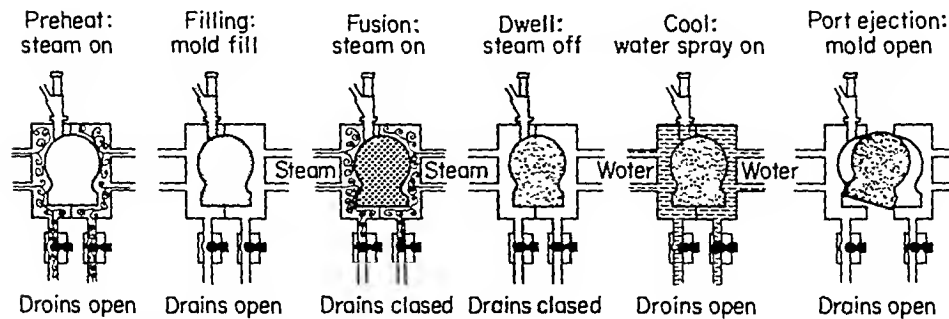


FIGURE 12-53
Molding polystyrene beads. (Reproduced by permission, copyright by The Dow Chemical Co., 1966.) [57.]

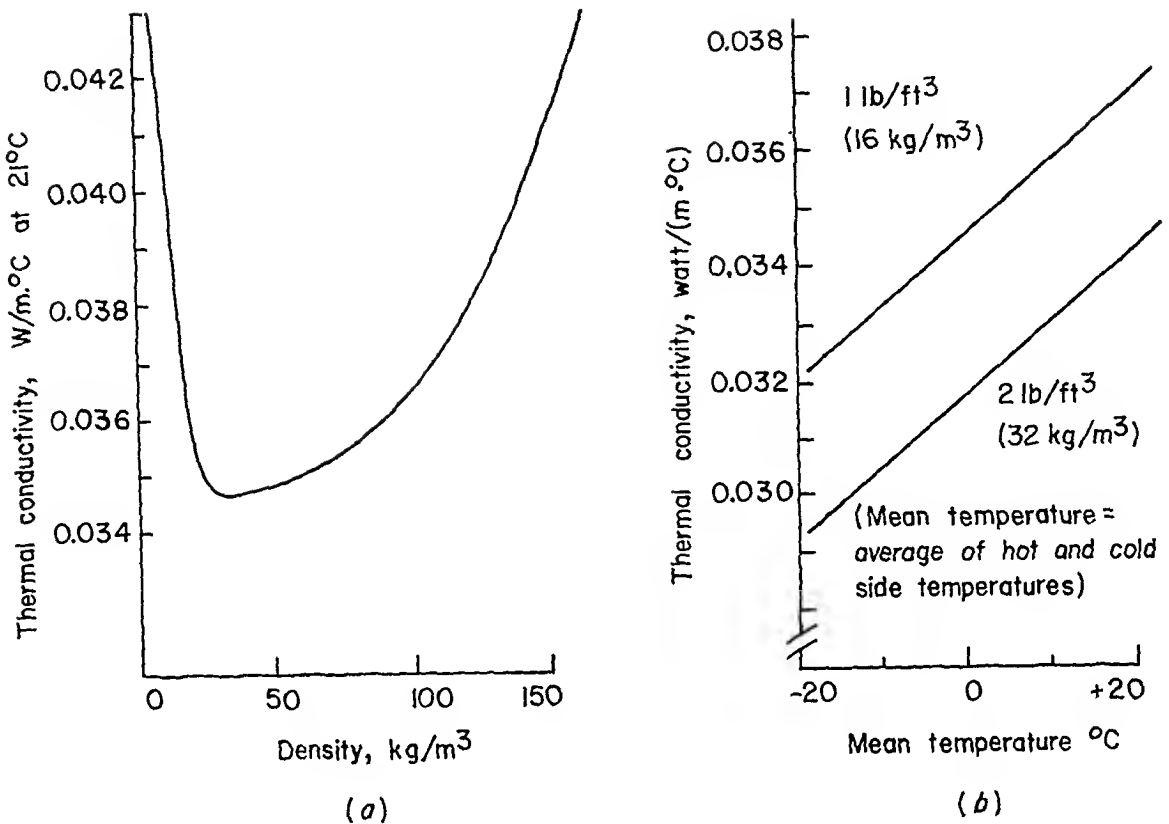


FIGURE 12-54

Thermal conductivity of expanded polystyrene beads as a function of (a) density, and (b) mean temperature for two densities (Reproduced by permission, copyright by The Dow Chemical Co., 1966.) [57].

transferred into the mold. The melt foams and fills the mold at a relatively low pressure (200 to 400 psi, that is, 1.3 to 2.6 MPa) compared to the much higher pressure in the accumulator. The lower pressures in the molds make the molds cheaper than those used for conventional injection molding. However, the cycle times are longer because the foam, being a good insulator, takes longer to cool. A major market for structural foams is in furniture. ABS and high-impact polystyrene are used to replace wood in seat panels, legs, chairs, and even some exterior panels for pianos. A wide variety of thermoplastics can be used. The trade-offs in deflection versus strength are illustrated in Table 12-11. Structural foams can also be made using a chemical blowing agent like those listed in Table 12-10 rather than an inert gas. A change in pressure or temperature on entering the mold triggers gas formation.

Sheet Forming

Often it is more economical to fabricate an article from a previously formed sheet than to start from raw pellets or slabs. In the case of thermoplastic materials the sheet is heated to a temperature at which it will deform under stress but not flow easily. This corresponds to the rubbery plateau region above T_g (and above T_m for a predominantly crystalline material). In this state the sheet readily deforms elastically. However, if the sheet is cooled below T_g (or T_m) in the deformed condition, it will remain there permanently. The process has many variations, as seen in Fig.

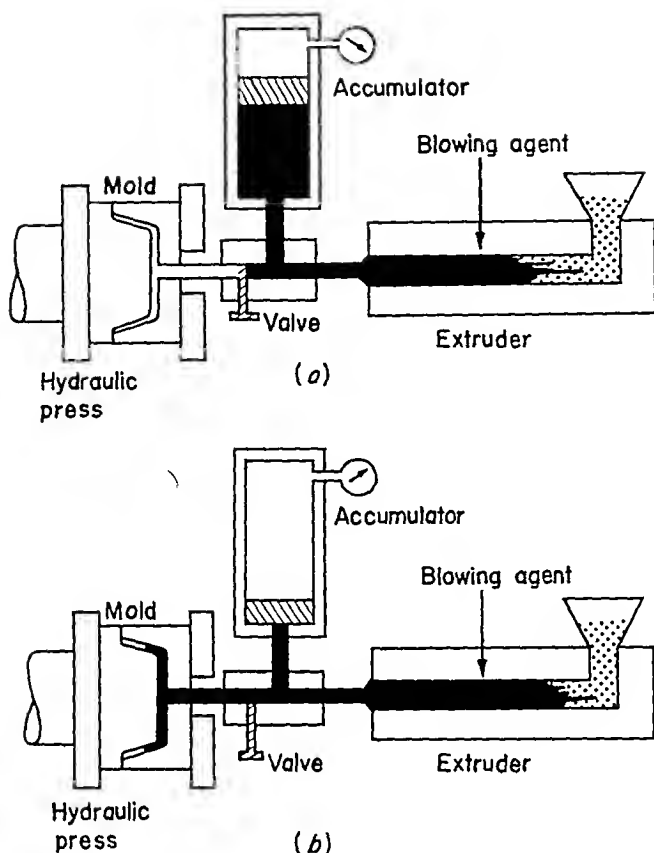


FIGURE 12-55

Structural foam process. (a) Filling the accumulator. The blowing agent—usually nitrogen—is injected into the melt in the extruder. The melt is passed into the accumulator, where it is maintained at a pressure and temperature high enough to prevent foaming until the predetermined charge is collected. (b) Filling the mold. The accumulator ram then injects the charge into the mold, where the reduced pressure allows the gas to foam the resin and drive it throughout the mold.

TABLE 12-11

Typical Properties of Three Plastics for Structural Foam

Property	General-purpose polypropylene		High-density polyethylene		High-impact polystyrene	
	Solid	Foam	Solid	Foam	Solid	Foam
Sample thickness, cm	0.38	0.635	0.38	0.635	0.44	0.635
Sample density, g/cm ³	0.902	0.6	0.962	0.6	1.04	0.7
Flexural strength, MPa	45	22	34	19	50	31
Flexural modulus, GPa	1.30	0.83	1.10	0.83	1.86	1.45
Deflection of simple beam with 10-cm span loaded with 2.3 kg, cm	0.36	0.23	0.50	0.32	0.20	0.11
Tensile strength, MPa	33	14	28	9.0	24	12
Coefficient of linear expansion, cm/cm·°C × 10 ⁶	9.4	9.4	12.1	12.1	9.0	9.0
Heat distortion temperature at 1.8 MPa load, °C	56	55	45	34	76	80
Mold shrinkage, %	0.018	0.015	0.020	0.018	0.010	0.008
Skin thickness, cm	0.38	0.080	0.38	0.080	0.44	0.080

12-56. In each case the sheet is first heated to a rubbery condition while firmly held in a frame. With thin sheets a few seconds exposure to a radiant heating panel may suffice. *Vacuum forming* can be used for making something like a contour map. The heated sheet is held above a plaster mold and sealed around the edges by a gasket. When a vacuum is applied through small holes in the mold, the sheet conforms to the

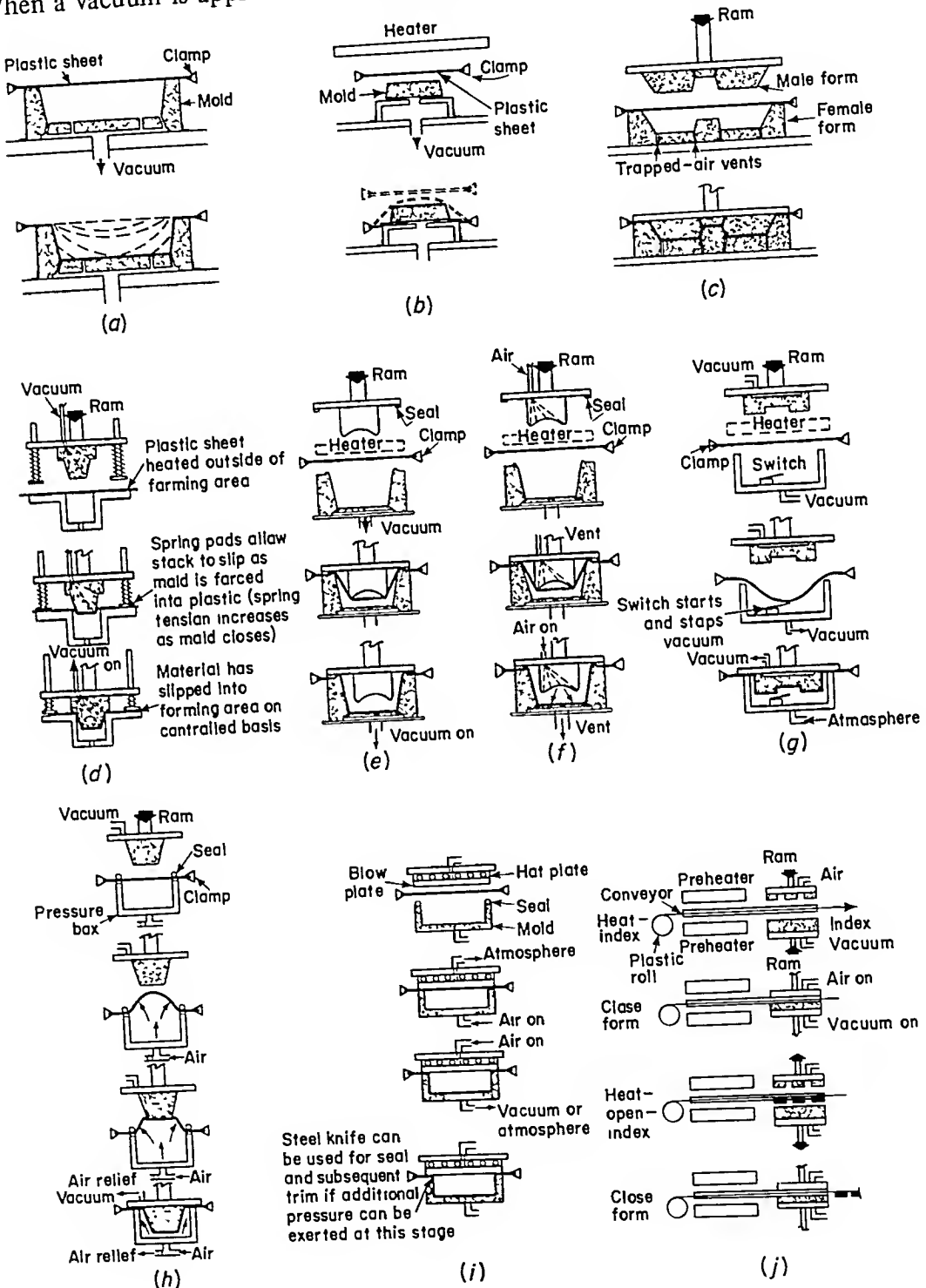


FIGURE 12-56

Ten methods of thermoforming [60]. (a) Straight vacuum; (b) drape; (c) match-mold; (d) slip-ring; (e) plug-assist, vacuum; (f) plug-assist, pressure; (g) snap-back, vacuum; (h) pillow; (i) trapped-sheet, contact-heat, pressure; (j) preheat, plug-assist, pressure forming.

mold and quickly cools to a temperature below T_g , since the mold surface, even of a poor conductor, has a heat capacity much greater than that of the thin sheet of plastic. The other methods illustrated use various combinations of pressure and vacuum as well as plugs and pads.

If the sheet has been subjected to biaxial orientation during extrusion (see Sec. 12-5, Flat Film, Sheet, and Tubing), heating above the deformation temperature will cause the sheet to shrink. A tight package can be made by wrapping an article in biaxially oriented sheet followed by a brief heat treatment. Such *shrink-packaging* with polypropylene film is used for lettuce and meats.

Postforming of thermoset sheets resembles metal forming. As opposed to the various sheet-forming methods, the dies are rugged, the stresses high, and the temperature often fairly high. Because thermoset materials already possess a dimensionally stable structure, it is necessary actually to break some covalent bonds and to form some new ones during postforming. The curvature is limited, since a sharp bend may crack the sheet. Paper laminates and vulcanized fiber are shaped by this method. Some common examples are trays, tote boxes, and countertops.

Some thermoplastic sheets can be *cold-formed*. It is possible to form sheets of some ABS polymers into dishes, louvers, and housings by application of sufficient pressure.

PROBLEMS

- 12-1. How might you expect the critical surface tension of a polymer to vary with the cohesive energy density? What factor could change the expected correlation? Compare the values of γ_c (Table 12-6) with values of δ_2 (Table 2-5).
- 12-2. The statement is often made that one cannot glue anything to polyethylene. Show that this is incorrect by applying a strip of cellophane tape to a film of polyethylene (a bread wrapper or freezer bag will do). From the force necessary to pull the tape off in shear, estimate the shear strength of the bond. Is the strength dependent on the time scale of the test? How?
- 12-3. A method for making rubber "thread" is to extrude and continuously vulcanize a flat sheet of rubber. The flat sheet is cut into individual strands with a rectangular cross-section. For a sheet 0.030-in thick, strands are cut 0.060 in wide. Calculate the denier and the strength in grams per denier if the rubber compound has a density of 0.85 g/cm^3 and a tensile strength of 3500 psi.
- 12-4. What are the similarities between transfer and injection molding? What are the differences? Injection molding has been used for rubber and thermosets recently. What major problems must be overcome? What relationship between flow temperature and cross-linking or polymerization temperature is desirable?
- 12-5. A candlemaker has decided to automate production of small wax candles by using a continuous extrusion-coating process such as that used to insulate wire. Cotton string will be used instead of wire, and the extrudate will be chopped into candles 6 in long and $\frac{1}{2}$ in in diameter. What problems might she expect? How might they be overcome? Should she hire a butcher and a baker as consultants? What experience have they had with extrusion?
- 12-6. Obtain a plastic bottle (an old bleach, shampoo, or cleanser bottle will do). Using a razor blade, cut two cross sections through the length of the bottle at right angles to each other (one down the front, one down the side). Observe and explain any variations in thickness.

- 12-7. Obtain a foamed polystyrene article made from expanded beads. Industrial packaging or a picnic hot-drink cup will do. From the weight and dimensions of a large piece, estimate the density. Break off some of the individual beads and estimate what the *original* bead diameter must have been before foaming.
- 12-8. How would you go about making rubber bands from vulcanized rubber?
- 12-9. A 60:40 emulsion copolymer of styrene and ethyl acrylate is proposed as a coating material (a latex paint). What difficulty is likely to be encountered? How might it be overcome?
- 12-10. Outline a suitable method of manufacture for (a) 100,000 ft of garden hose from plasticized poly(vinyl chloride), (b) 50,000 pocket combs from polystyrene, and (c) two boat hulls, each 15 ft long, from glass cloth and a solution of an unsaturated polyester in styrene monomer.
- 12-11. Describe the role of each of these ingredients within each system and classify each system as a paint, enamel, varnish, lacquer, or putty.

System A:

Linseed oil
Mineral spirits
Cobalt naphthenate
Calcium carbonate

System B:

Cellulose nitrate
Methyl ethyl ketone
Titanium dioxide

System C:

Tall oil fatty acids
Ethylene glycol
Glycerol
Phthalic anhydride

Mineral spirits

Lead naphthenate

System D:

Shellac
Ethyl alcohol

} cooked together but
describe each separately

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13

CARBON CHAIN POLYMERS

13-1 INTRODUCTION

In considering manufacturing processes for individual polymers, it is convenient to group them in two broad classes, those with backbones containing only carbon and those with backbones containing additional atoms such as oxygen, nitrogen, sulfur, or silicon. Polymers in the first class are made by addition reactions at the double bond (or 1,4-polymerization at a conjugated double bond system). Polymers in the second class can be made by a variety of reactions including condensation and ring scission.

Two of the major polymer-based industries are found to depend more on one class than the other. The rubber industry uses both carbon chain and heterochain polymers. A generic classification of elastomers with the abbreviations suggested by the American Society for Testing Materials (ASTM) indicates no bias towards carbon chain polymers (Table 13-1). However, the seven heterochain rubbers listed probably constituted less than 5% of the total rubber produced in 1978. The reason for this situation appears to be economic and historical rather than fundamentally physical or chemical. Heterochain polymers of excellent strength, resilience, and durability have been designed, but never at a price that attracted widespread use. The generally conservative nature of an industry founded on one natural polymer has been another strong deterrent to innovation.

The fiber industry presents a bias towards heterochain polymers. Once again, a listing of the generic names of the man-made fibers (Table 13-2) includes both classes. Since rayon, acetate, nylon, and polyester are the fibers produced in largest volume, heterochains apparently dominate. In the case of fibers, one can see indications of change, because the acrylics, modacrylics, and olefins are growing in importance. The reason for the dominance by heterochain polymers does have a physical and chemical basis. The *sine qua non* of fibers is a high T_m together with a reasonable

TABLE 13-1
Generic Classification of Some Commercial Elastomers [1]

ASTM designation	Common or trade name	Chemical designation
IR	Synthetic natural rubber	Synthetic polyisoprene
IIR	Butyl, Chloro-butyl	Isobutylene-isoprene
ACM	Acrylic	Polyacrylate
AU*	Urethane (UR)	Polyurethane (polyester)
EU*	Urethane (UR)	Polyurethane (polyether)
BR	CBR, PBd	Polybutadiene
CO*	Hydrin (CO, ECO)	Polyepichlorohydrin
CR	Neoprene	Chloroprene
CSM	Hypalon (HYP)	Chlorosulfonyl polyethylene
EPM	EP elastomer	Ethylene propylene copolymer
EPDM	EP elastomer	Ethylene propylene terpolymer
ET*	Thiokol A	Ethylene polysulfide
EOT*	Thiokol B	Ethylene ether polysulfide
FKM	Viton, Fluorel, Kel-F	Fluorinated hydrocarbon
NBR	Buna N, Nitrile	Butadiene-acrylonitrile
SBR	GR-S, Buna S	Styrene-butadiene
VMQ*	Silicone	Poly(dimethylsiloxane) with vinyl groups
PVMQ*	Silicone	Silicone rubber having methyl, phenyl, and vinyl groups
FVMQ*	Silastic LS	Silicone rubber having methyl, vinyl, and fluorine groups
CM	Plaskon CPE	Chlorinated polyethylene
NR	Natural rubber	Natural polyisoprene
YSBR	Kraton, Solprene	Block copolymers of styrene and butadiene

*Heterochain polymers.

degree of crystallinity on stretching (drawing). The heterochain structure is higher in polarity than the carbon chain, and it can often be tailored to a suitable chain stiffness. The high polarity of the nitrile group in acrylics and the remarkable regularity of isotactic polypropylene permit these carbon chain polymers to compete successfully.

Inevitably, some polymers refuse to fit in one class or the other. The polyxylenes (Sec. 12-4) are carbon chain polymers except that the phenylene group is in the backbone. Another exception is the ladder polymer from polyacrylonitrile (Sec. 3-5), which starts as a carbon-chain polymer but is converted by oxidation to a polycyclic heterochain structure.

Within each of the two major classes the polymers have been arranged in families. Although some properties and uses are mentioned, more detail on individual polymers is to be found in App. 5.

13-2 THE POLYOLEFINS

Ethylene and propylene from petroleum-refining operations or from natural gas are the cheapest raw materials for polymer production. Aside from being the starting

TABLE 13-2
Classification and Properties of Principal Man-Made Fibers[†] [2]

Fibers	Characteristic properties
<i>Cellulosic fibers</i>	
Rayon—composed of regenerated cellulose from wood and cotton fiber [*]	Easy to dye and finish, rayon offers high moisture absorption, flexibility, soft hand, good drape, minimum tendency to develop static charges
Acetate and triacetate—composed of regenerated cellulose from wood and cotton fiber that has been treated with acetic acid [*]	Easy to dye, supple, fast drying, good drape, wrinkle-resistant; heat-set triacetate has high resistance to shrinking, stretching and wrinkling
<i>Synthetic polymer fibers (noncellulosic)</i>	
Acrylic—at least 85% by weight acrylonitrile-based polymer.	Warmth without weight, durable, soft hand, shape retention, resistant to sunlight, weather, oil and chemicals
Modacrylic—at least 35% but not more than 85% acrylonitrile-based polymer	Resemble acrylic fibers; self-extinguishing when exposed to flame
Anidex—a manufactured fiber in which the fiber-forming substance is any long-chain synthetic polymer composed of at least 50% by weight of one or more esters of a monohydric alcohol and acrylic acid	Imparts permanent stretch and recovery properties of fabrics
Aramid—a manufactured fiber in which the fiber-forming substance is a long-chain synthetic polyamide in which at least 85% of the amide linkages are attached directly to two aromatic rings	High strength and high temperature stability
Novoloid—a manufactured fiber containing at least 85% by weight of a cross-linked novolac	Converts to carbon fiber at high temperatures; used in flame-protective garments
Nylon—a manufactured fiber in which the fiber-forming substance is a long-chain synthetic polyamide in which less than 85% of the amide linkages are attached directly to two aromatic rings	Great strength, chemical resistance, high elasticity, durability, and range of dyeability
Nytril—a manufactured fiber containing at least 85% of a long-chain polymer of vinylidene dinitrile where the vinylidene dinitrile content is no less than every other unit in the polymer chain	Soft and resilient, used in sweaters
Olefin—at least 85% by weight ethylene, propylene, or other olefin-based polymers; polypropylene most common	Lightest man-made fiber, low moisture absorption, high strength, chemical and soil resistance
Polyester—at least 85% by weight of an ester based on dihydric alcohol and terephthalic acid [*]	High strength, resistance to stretching and shrinking, dyes well, resists chemicals, crisp and resilient both wet and dry, fabric can be heat-set

(See footnotes on page 384.)

TABLE 13-2 (Continued)
Classification and Properties of Principal Man-Made Fibers[†] [2]

Saran—at least 80% by weight vinylidene-chloride-based polymer	Resistance to chemicals, sunlight, and outdoor exposure; nonflammable
Spandex—at least 85% by weight polyurethane*	Easily dyed; strength and durability; high elastic recovery, resistance to chemicals
Vinal—a manufactured fiber in which the fiber-forming substance is any long-chain synthetic polymer composed of at least 50% by weight of vinyl alcohol units and in which the total of the vinyl alcohol units and any one or more of the various acetal units is at least 85% by weight of the fiber	High resistance to chemicals
Vinyon—at least 85% by weight vinyl-chloride-based polymer	Resistance to chemicals; softens at low temperatures
<i>Fibers from nonfibrous natural substances</i>	
Glass—composed of silicon dioxide and other components drawn from molten state	Great strength and resistance to heat, flame and most chemicals; will not shrink, stretch, or absorb water
Metal—various metals and alloys drawn to fine-diameter fiber	Properties similar to metals from which they drawn
Rubber—natural or synthetic rubber drawn into fiber form	Elastic, often is a core around which other fibers are wrapped
Azlon—manufactured from naturally occurring proteins in corn, peanuts, and milk*	Soft feel, blends with other fibers, used like wool

*Heterochain polymers.

[†]This tabulation is based on the Federal Trade Commission's Textile Fiber Products Identification Act, which assigns generic names to the various types of man-made fibers.

materials for a variety of other monomers, they are combined in an impressive array of products (Table 13-3). Branched polyethylene, its chlorosulfonated, rubbery derivative, and butyl rubber date back to the 1930s and 1940s. The 1950s saw the introduction of linear polyethylene and isotactic polypropylene. Copolymers of ethylene with propylene and with polar monomers came along in the 1960s, as did the isotactic polymer of 4-methylpentene-1.

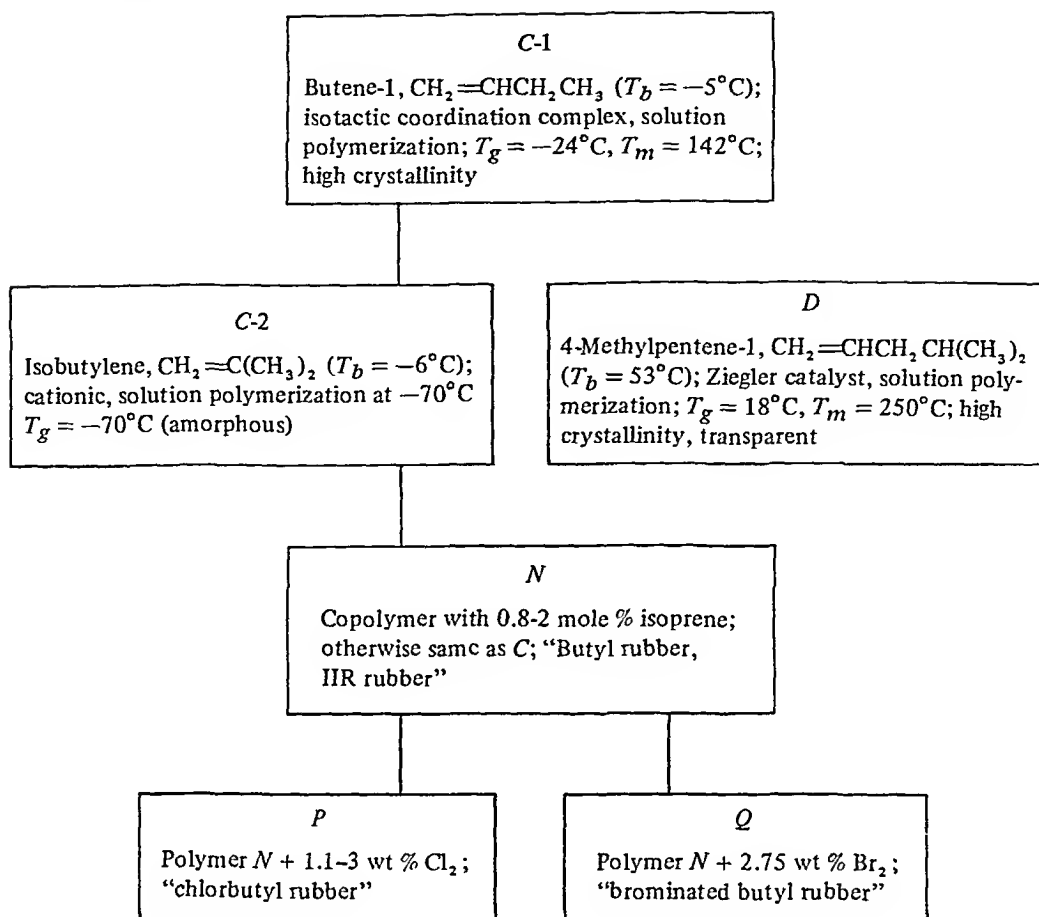
The range of properties that can be achieved within the olefin family goes from highly crystalline, linear polymers of high T_m to completely amorphous, rubbery materials that are branched or cross-linked (in the case of cross-linked butyl, EPM, and EPDM rubbers). Even in the homopolymers of ethylene, mechanical behavior will be affected by molecular weight and branching (Fig. 13-1). A high-molecular-weight, linear polyethylene is dense, reflecting its high crystallinity. Also, it is highly viscous, almost rubbery, in the melt at, say 200°C. Branching decreases crystallinity, as does copolymerization. Molecular weights of a few hundred to ten thousand are typical of the naturally occurring waxes recovered from petroleum.

The free-radical polymerization of ethylene requires extremely high pressures. In a typical scheme (Fig. 13-2) 10 to 30% of the monomer might be converted in a single pass at 1000 to 3000 atm and 100 to 200°C. While a peroxide might be introduced, a small amount (0.05%) of oxygen is an effective initiator. Under these condi-

TABLE 13-3
The Polyolefins

<i>A</i> Ethylene, $\text{CH}_2=\text{CH}_2$ ($T_b = -104^\circ\text{C}$) (Linear) coordination complex, solution polymerization; $T_g = -120^\circ\text{C}$, $T_m = 137^\circ\text{C}$; high crystallinity (Branched) free-radical, bulk polymerization, high pressure; $T_g = -120^\circ\text{C}$, $T_m = 110^\circ\text{C}$; medium crystallinity	<i>B</i> Propylene, $\text{CH}_2=\text{CHCH}_3$ ($T_b = -48^\circ\text{C}$); coordination complex, solution polymerization; $T_g = -18^\circ\text{C}$, $T_m = 176^\circ\text{C}$; high crystallinity
<i>E</i> Copolymer with 10-40 wt % vinyl acetate; free-radical, bulk polymerization; $T_s = 45$ to 80°C	<i>K</i> Block copolymer with high propylene; coordination complex, solution polymerization; $T_s = 122$ to 136°C; high crystallinity "polyallomers"
<i>F</i> Copolymer with 10-40 wt % ethyl acrylate; free-radical, bulk polymerization; $T_s = 45$ to 80°C	<i>L</i> Random copolymer with 50 to 65 wt % propylene; coordination complex, solution polymerization; $T_g = -50^\circ\text{C}$ (amorphous); "EPM rubber"
<i>G</i> Copolymer with acrylic or methacrylic acid followed by neutralization with base; free-radical, bulk polymerization; $T_s = 70^\circ\text{C}$; medium crystallinity; transparent "ionomers"	<i>M</i> Random terpolymer like copolymer + about 3% nonconjugated diene; coordination complex, solution polymerization; $T_g = -50^\circ\text{C}$ (amorphous); "EPDM rubber"
<i>H</i> Polymer + Cl_2 (30 to 45 wt % Cl_2 in product); $T_g = -20^\circ\text{C}$ to -30°C (amorphous); "chlorinated polyethylene" <i>J</i> Polymer + Cl_2 + SO_2 (27 wt % Cl_2 and 1.2% S in product); $T_g = -55^\circ\text{C}$ (amorphous); "chlorosulfonated polyethylene," "CSM rubber"	

T_b = boiling temperature
 T_g = glass transition temperature
 T_s = softening temperature
 T_m = melting temperature

TABLE 13-3 (Continued)
The Polyolefins

tions the ethylene is well above its critical pressure and temperature and the polymer is dissolved. Stirred reactors have been used, but there are obvious advantages in using a tubular reactor at high pressures. A peristaltic flow in which ethylene is continuously pumped into the tube and product periodically released from the other end is used to approximate a plug flow through the tube and decrease the buildup of polymer on the walls. In a single-train system with a capacity of 100×10^6 kg/yr, the tube might be over 1 km long with an inside diameter of 5 cm and an outside diameter of 15 cm. In any kind of reactor the chain transfer between growing polymer and "dead" chains occurs at high pressures, resulting in the branched structure discussed in Sec. 4.4. The same apparatus can be used to produce copolymers of ethylene with polar monomers such as vinyl acetate and ethyl acrylate. As the ethylene content goes down, the crystallinity decreases and room-temperature flexibility increases. Some items in which this controlled degree of flexibility is useful are tubing, protective coatings (waxes and polishes), adhesives, and shoe soles. Copolymerization with carboxylic acids followed by neutralization with a base (usually NaOH) gives the class of *ionomers*. Although still crystalline, the spherulite size is decreased, making films of ionomers much more transparent than those of polyethylene. As might be expected,

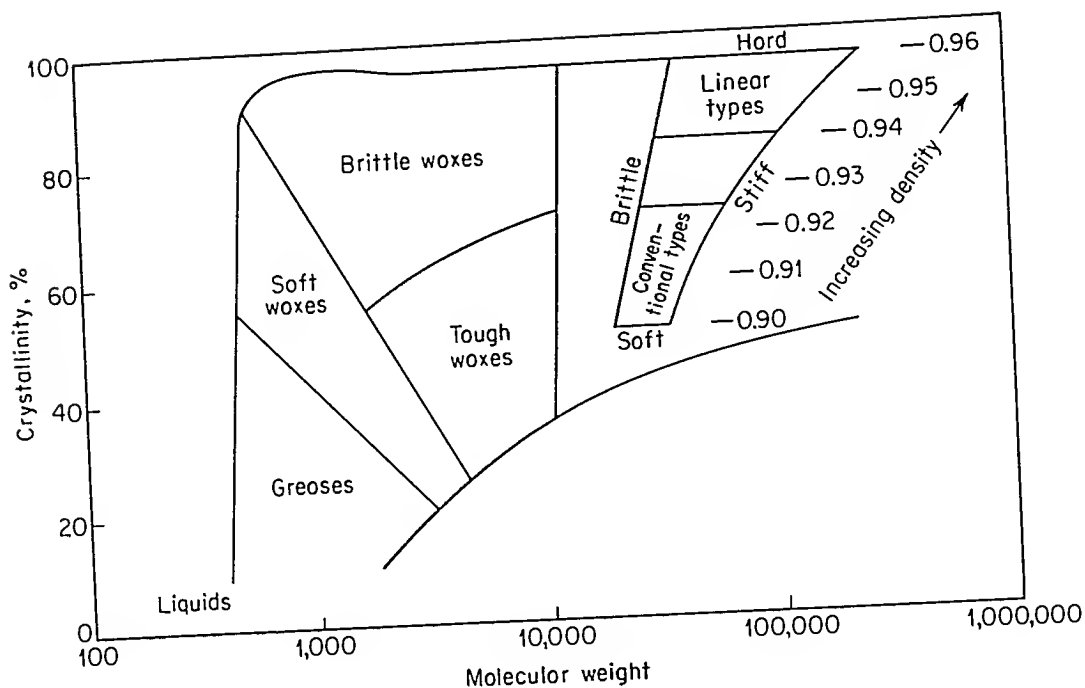


FIGURE 13-1
Relationships between crystallinity, molecular weight, and mechanical properties of polyethylene [3]. (After Kratz and Lyle, *Encyclopedia of Chemical Technology*, First Suppl., Interscience, 1957.)

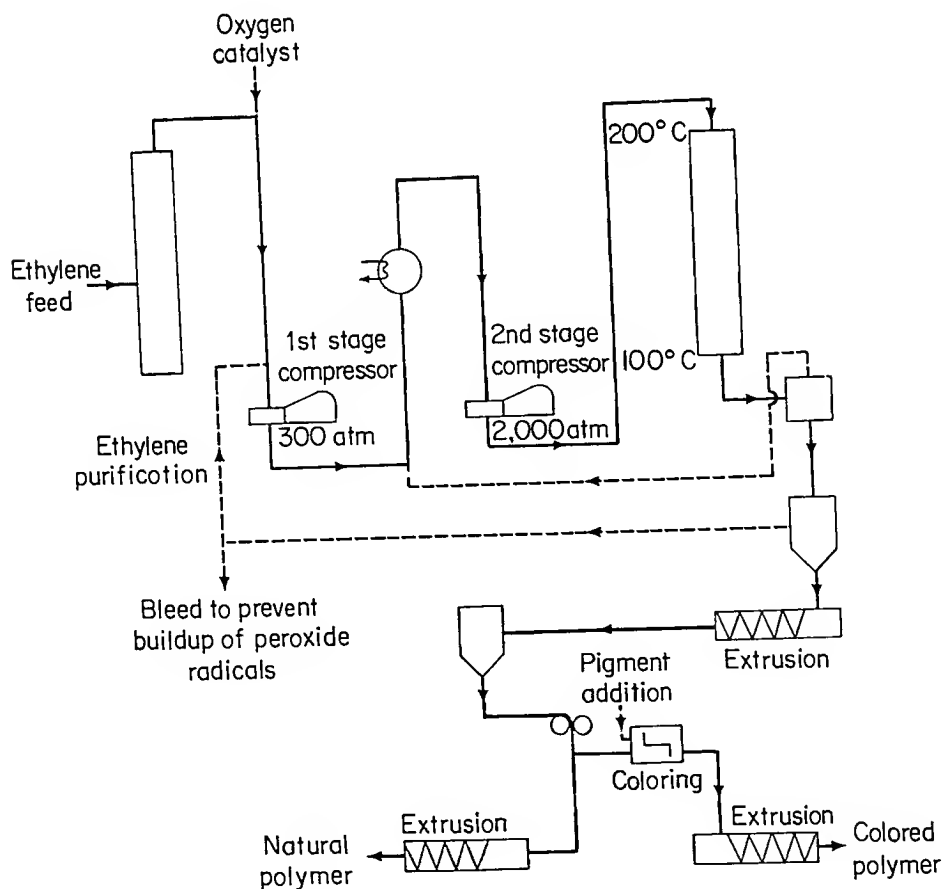


FIGURE 13-2
Simplified flow scheme for the high-pressure polymerization of ethylene [4].

the ionic groups facilitate adhesion and printing. The ionic groups act as somewhat labile cross-links in the melt, so that ionomer sheets are rubbery and can be vacuum-formed more easily than polyethylene. It is possible also to graft an ionic monomer like acrylic acid on a "dead" polyethylene or polypropylene. Under these circumstances the ionic groups will probably be clustered at the grafting points rather than randomly distributed as they would be in a random copolymerization. Thus, while both products would combine the main features of a polyolefin with ionic character, they may well differ in their applicability for a given end use.

Both the Ziegler-type catalysts and supported metal oxides (Phillips process) are capable of producing linear polyethylene. Both systems use a hydrocarbon solvent, are sensitive to water and polar compounds, require catalyst residue removal for the best electrical and optical properties, operate at moderate pressures, and are relatively slow. Reactor residence times of several hours are typical. As indicated in the flow sheet (Fig. 13-3), the metal oxide might be CrO_3 supported on Al_2O_3 (or a silica-alumina base), and polymerization takes place at a pressure of a few hundred psi and a temperature high enough that the polymer dissolves to form a dope up to a concentration of about 10%. The Ziegler process (Fig. 13-4) may be carried out at a lower temperature and, consequently, a lower pressure. Depending on the solvent, the molecular weight, and the temperature, the polymer may stay in solution or precipitate to form a slurry. In the Ziegler process hydrogen is an effective chain transfer agent and can be added to regulate the molecular weight. In the Phillips process the molecular weight is strongly temperature-dependent, increasing about threefold as the temperature is decreased from 170 to 140°C. Generalizations about these two major processes are dangerous, since hundreds of significant variations in catalyst composition are recorded in the literature and no two companies use exactly the same recipe.

Gas-phase polymerization for ethylene was commercialized in 1968. Elimination of solvent recovery and catalyst removal as process steps give significant economies. In one installation [5] with a capacity of 100×10^6 kg/yr, the fluid bed reactor

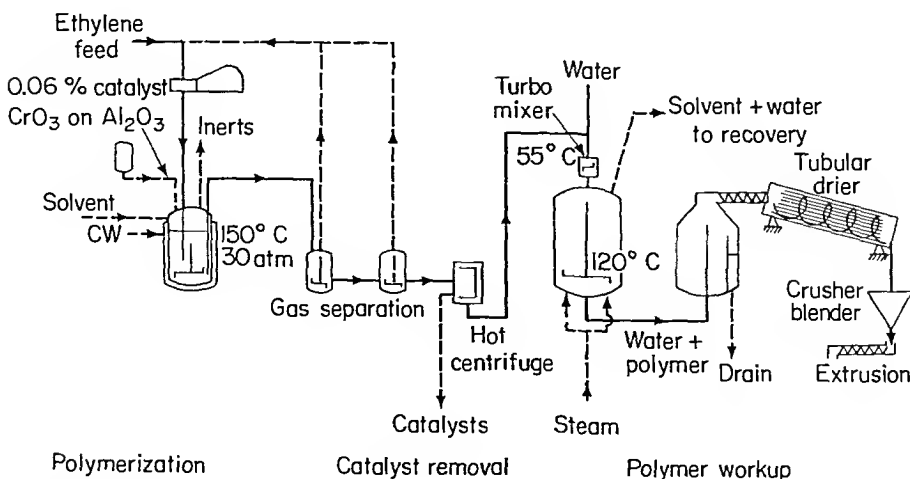


FIGURE 13-3

Flow scheme for ethylene polymerization by the Phillips process [4].

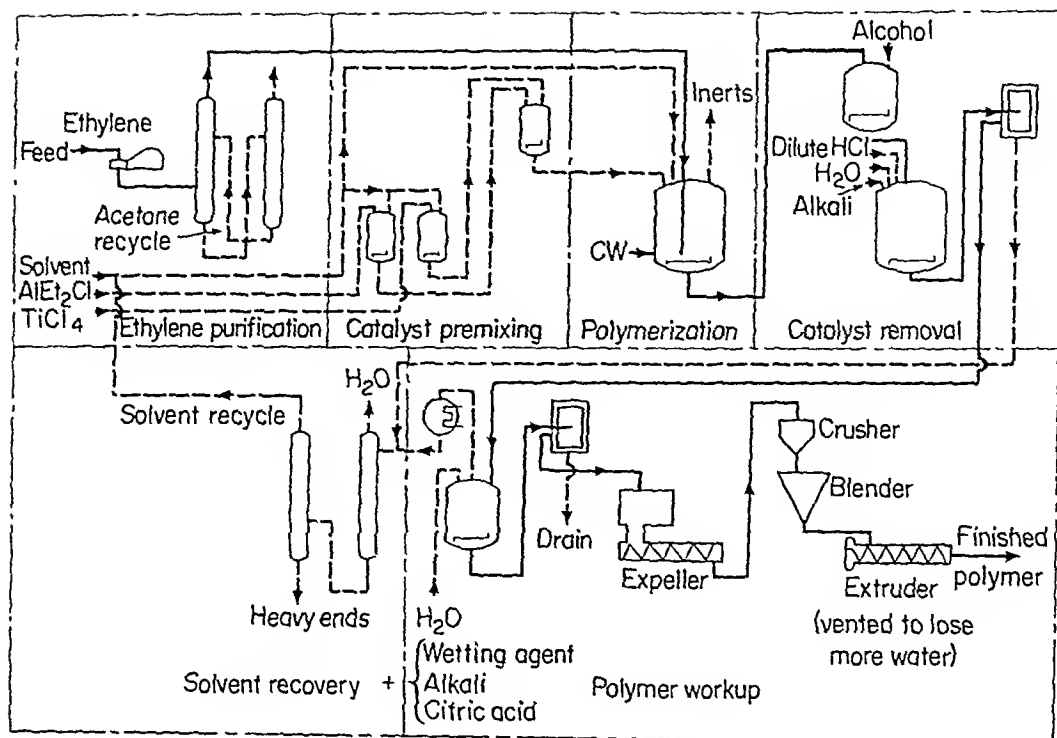


FIGURE 13-4

Flow scheme for ethylene polymerization by the Ziegler process [4].

(Fig. 13-5) has a diameter of 4.3 m (14 ft). Purified ethylene and powdered catalyst (modified chromia on silica) are fed continuously, and polyethylene fluff is removed intermittently from the reactor through a gas-lock chamber. Reactor pressure is about 20 atm and the temperature is 85 to 100°C. Heat of polymerization is removed as the gas is circulated through external coolers. Only about 2 or 3% of the monomer is converted per pass, but overall monomer loss is kept below 1% of the feed by recycling. The growing particles remain in the reactor 3 to 5 h where they attain a final diameter of about 500 μm . Since as much as 600,000 kg of polymer can be formed per kg of chromium, catalyst removal is not necessary for many applications. Molecular weight can be decreased using hydrogen as a chain transfer agent, and short-chain-branching can be introduced with 1-butene to decrease crystallinity.

Recently the process has been modified to produce a polyethylene similar in density to the older, high-pressure-process material [6]. In the trade the terms HDPE (high-density, or linear, polyethylene) and LDPE (low density, or branched, polyethylene) are now being supplemented by LLDPE (linear, low-density polyethylene). While all the properties of the high-pressure polymer are not achieved by the new material, the economics of the low-pressure, solvent-free process are such that about half the volume in markets once dominated by branched LDPE will be in competition with LLDPE. At least in the immediate future few new high-pressure plants are likely to be built.

The Ziegler system has been used to produce a number of stereoregular polymers. Isotactic and syndiotactic polymers of many olefins have been made in the laboratory. Two of these, isotactic polypropylene and poly(4-methylpentene-1), are available commercially. Production parallels the scheme of Fig. 13-4. To obtain a

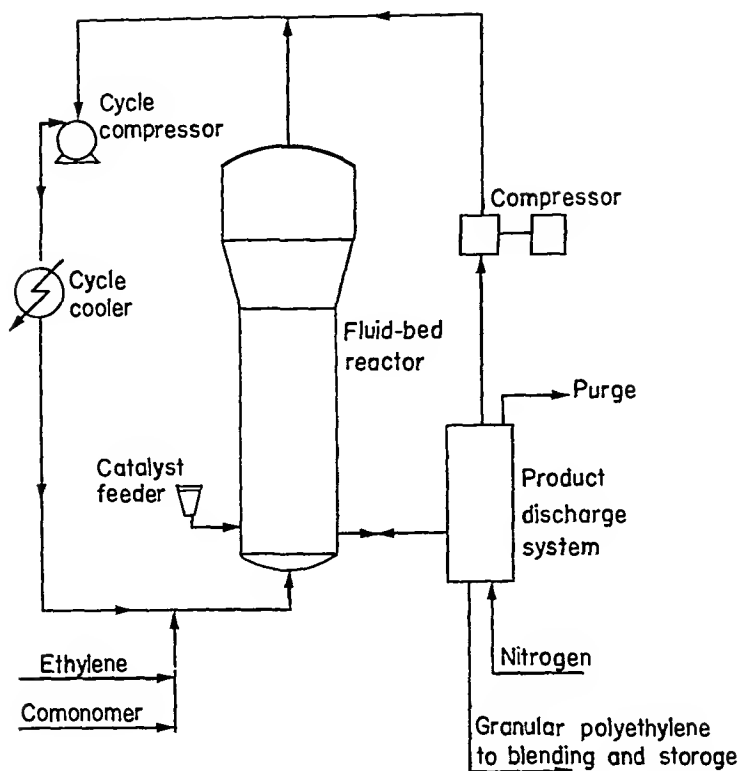
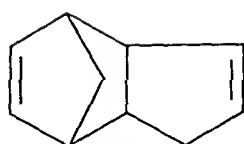


FIGURE 13-5
Gas-phase polymerization of ethylene [6].

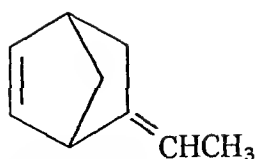
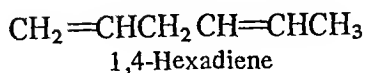
polymer of maximum isotactic content, the dope may be precipitated in such a way as to leave the atactic portion behind in solution.

Polyallomers are block copolymers of propylene with small amounts of ethylene. The lifetime of a single growing chain apparently is long enough that blocks can be achieved by a rhythmic alternation of ethylene and propylene in the monomer feed. The materials still are highly crystalline. However, when a random copolymer is made with almost equal amounts of ethylene and propylene, the product is amorphous and rubbery (*EPM* rubber). Peroxides can be used to cross-link either polyethylene or *EPM* by hydrogen atom abstraction followed by radical combination. The mechanism was outlined in Sec. 11-3.

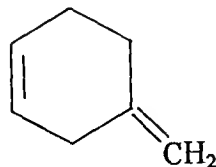
The cross-linking is done in a separate operation after the polymer has been made. The rubber is compounded and molded or extruded into its final shape before being cured. By incorporating a third monomer, which contributes a favored cross-linking site, a wider variety of cross-linking agents can be used. Some nonconjugated dienes are especially useful, since only one double bond polymerizes, leaving a pendant unsaturation that is reactive with the sulfur and sulfur-bearing vulcanizing systems long used in the rubber industry. Some dienes used to the extent of about 3% in *EPDM* (ethylene-propylene-diene monomer) rubber are:



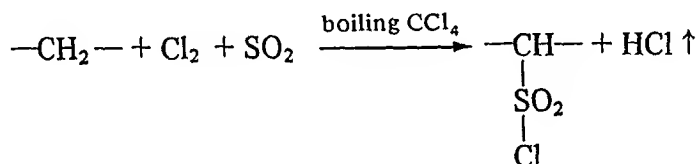
Dicyclopentadiene

5-Ethylidene-
2-norbornene

1,4-Hexadiene

5-Methylene-2-
norbornene

A rubbery material can be made directly from branched polyethylene by postchlorination. A major use of this material is as a polymeric plasticizer for poly(vinyl chloride). If SO_2 is added during chlorination, chlorosulfonic groups are added. These act as preferred cross-linking sites when the polymer is heated with a metal oxide and a source of water.



In a typical commercial polymer there is one chlorosulfonyl group for each 200 backbone carbon atoms. Magnesia (MgO) and a hydrogenated wood resin (as a source of H_2O) can be used as a cross-linking system.

There are some dramatic contrasts between the cationic polymerization of isobutylene and the free-radical and coordination complex (both Ziegler and Phillips) methods. Few free-radical processes can be operated below room temperature. Even when the radicals can be generated, the rate of propagation is low. On the other hand, the cationic growth of isobutylene proceeds rapidly at -65°C . Like the coordination complex systems, most cationic catalysts are inactivated by water. Unlike them, however, the radical life is short, so that the long reactor residence times are not necessary. The major engineering problem becomes that of heat removal at a low temperature. Cooling coils containing liquid ethylene are used inside the reactor (Fig. 13-6). The continuous feed to the reactor consists of two solutions, the monomers (25% isobutylene, 2 to 3% isoprene, balance methyl chloride) and the catalyst (0.4% AlCl_3 in methyl chloride). About 3 parts of the latter are sprayed into 10 parts of the former solution. The exothermic reaction is almost instantaneous, and a slurry of fine polymer particles overflows into an agitated flash tank with an excess of hot water. The methyl chloride and any unreacted hydrocarbons are flashed off and sent to a recovery system. An antioxidant and a lubricant (zinc stearate) are added to the slurry in the flash tank also. Screening, filtering, and drying in a tunnel dryer are

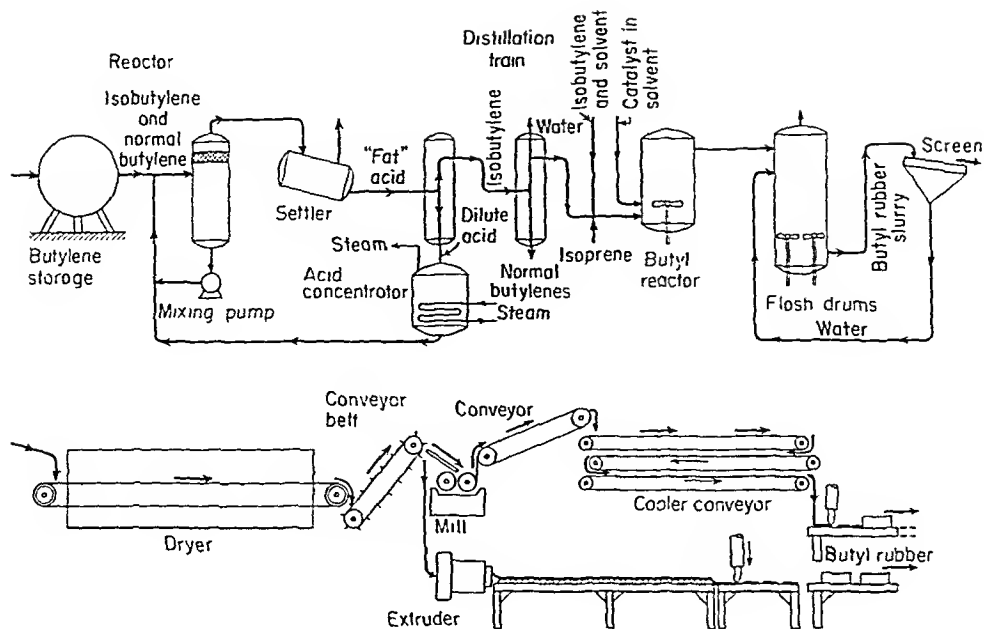
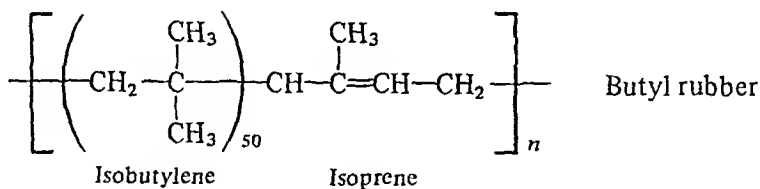


FIGURE 13-6

Butyl rubber production [7].

followed by a forming operation and packaging. The isoprene is used to provide a preferred cross-linking site. The copolymer has been chlorinated and brominated to



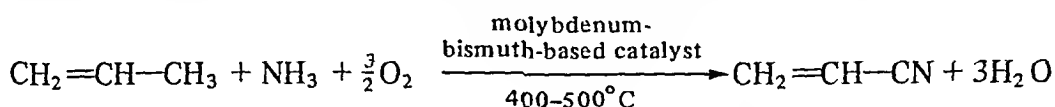
provide a different reactive group for cross-linking. Metal oxide cross-linking with a halogenated group gives a structure which is more stable at high temperatures than the sulfur cross-link usually employed with residual unsaturation.

Use Pattern

Blow-molded bottles from polyethylene (squeeze bottles and detergent and bleach bottles) and packaging film are everyday examples of large-volume uses (Table 13-4). Except for butyl rubber and chlorosulfonated polyethylene, the polyolefins are not easily dissolved at room temperature, so they have not been widely used in solvent coatings or adhesives. Melt coating or laminating of polyethylene on paper or cardboard is important for making containers for milk and other liquids. Butyl rubber had a large market in inner tubes before the advent of the tubeless tire. An all-butyl tire was offered for a time. Tires still make use of nonstaining polyolefin rubbers for white sidewalls. Tires based on EPDM have been made on an experimental basis.

13-3 THE ABS GROUP

Homopolymers and interpolymers from acrylonitrile, butadiene, and styrene offer a wide range of properties (Table 13-5). It has been pointed out (Sec. 1-2) that the synthetic rubber program during World War II established almost overnight a tremendous capacity for styrene and butadiene. Butadiene is made by the dehydrogenation of butane or butene from petroleum. Since benzene can be made from petroleum by catalytic reforming, much styrene owes its origin to petroleum too. Benzene is alkylated with ethylene (AlCl_3 catalyst) and dehydrogenated to make styrene. The third member of the ABS triumvirate, acrylonitrile, can be made by several routes. A single-stage catalyzed reaction of propylene with ammonia and oxygen is popular:

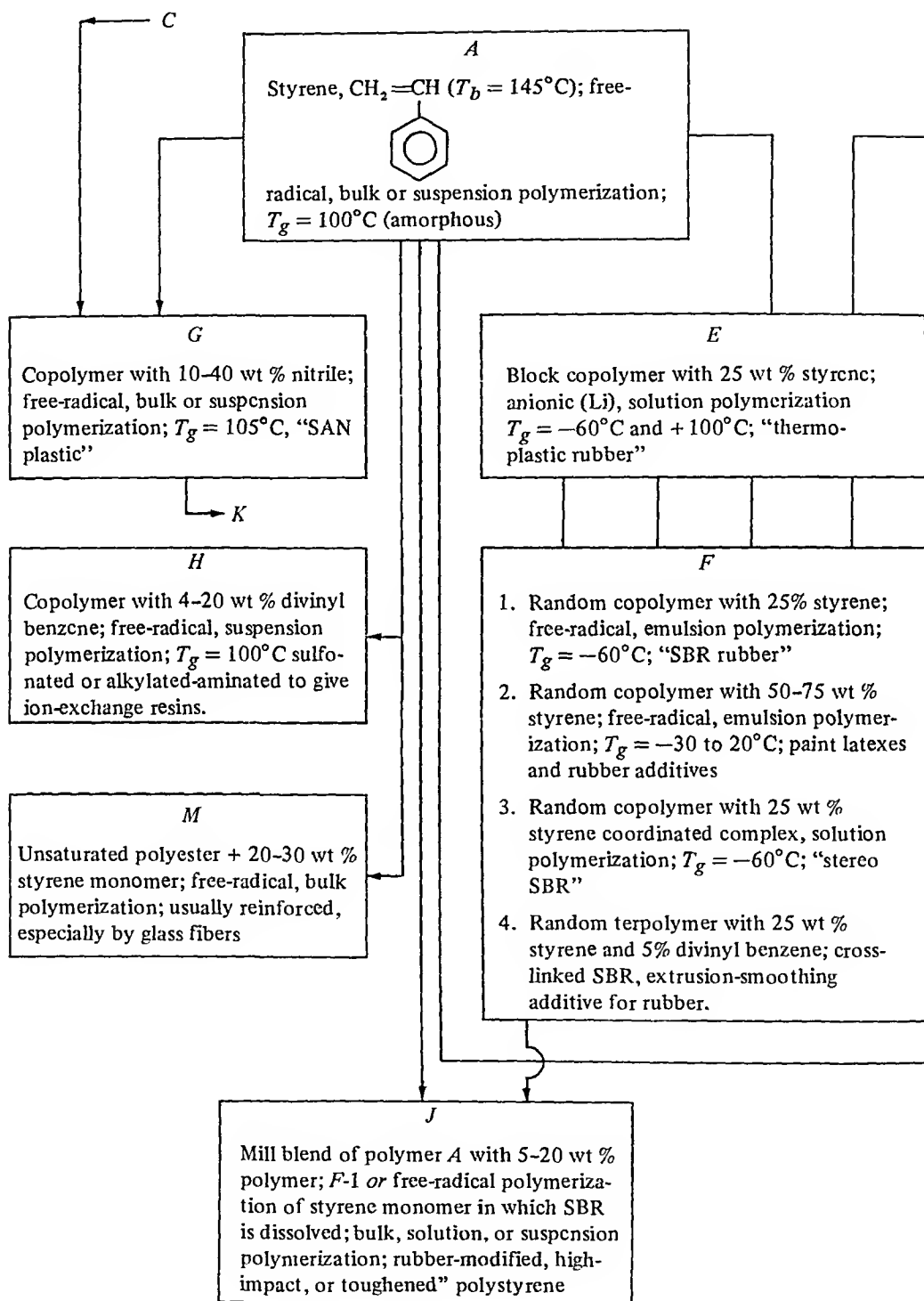


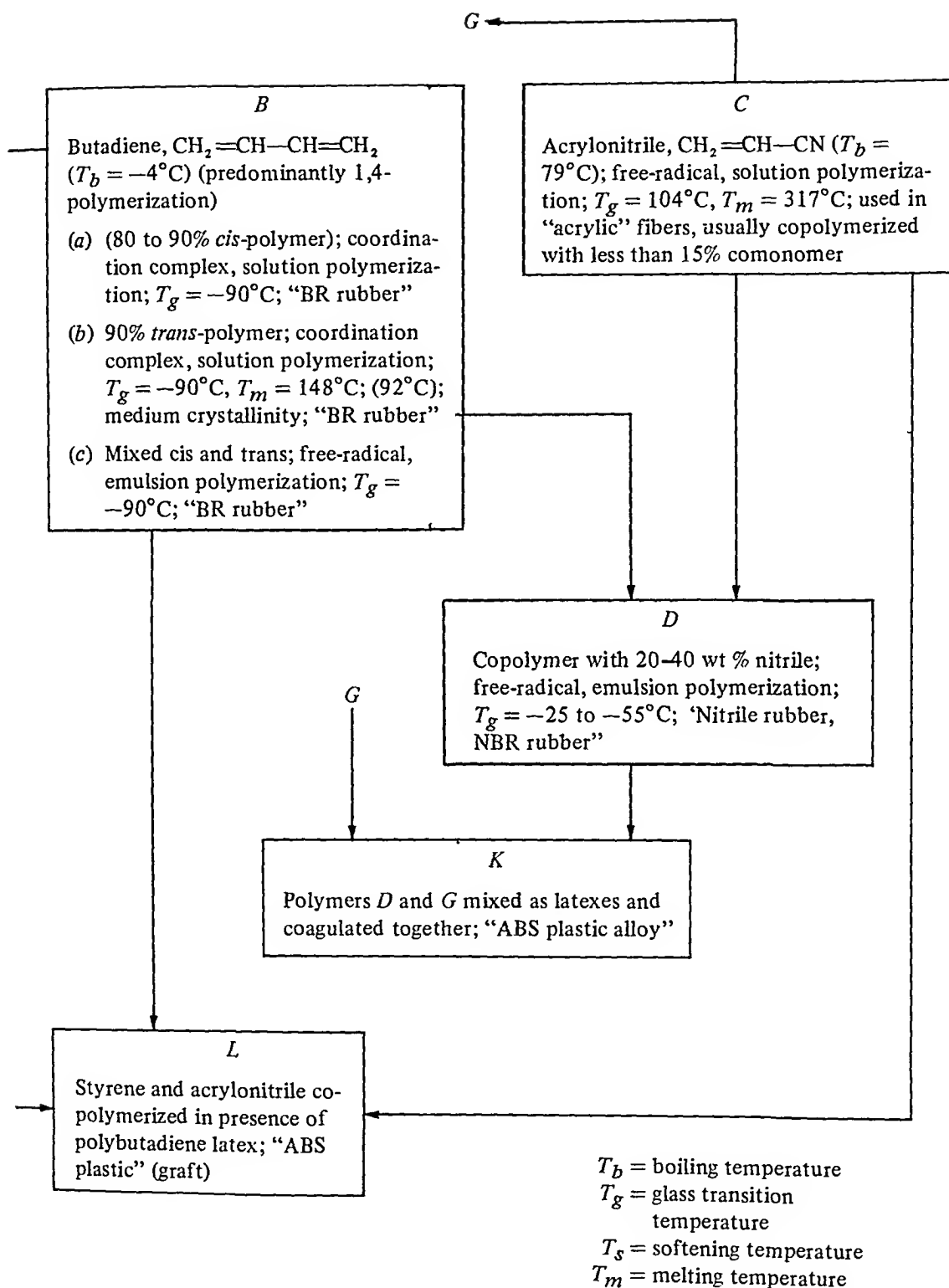
A discussion of the stereoregular homopolymers of butadiene is delayed until Sec. 13-4. Although the monomer also is homopolymerized by one producer by a free-radical, emulsion technique, the styrene copolymer (SBR) affords a more complete example (Fig. 13-7). A continuous emulsion polymerization makes use of a series of 12 7000-gal reactors, each 20 ft tall and 90 in in (inside) diameter. Each reactor is compartmented and stirred, so that the emulsion passes from one end of the train to the other in a kind of plug flow. Residence time in each reactor is 1.0 to 1.25 h, and the heat removed in each may be as high as 132,000 Btu/h. Either "hot" rubber is made with a peroxide initiator at 50°C or "cold" rubber is made with a redox couple at 5°C . A chain transfer agent, dodecyl mercaptan, is added to regulate molecular weight. After reaching a conversion of about 75%, the reaction is short-stopped by the addition of hydroquinone, and unreacted monomers are removed without coagulation in vacuum flash tanks and falling-film strippers. The relative reactivities are such that butadiene is consumed more rapidly than styrene ($r_1 = 1.4$, $r_2 = 0.8$). Conse-

TABLE 13-4
End Use Pattern for Polyolefins

Polymer*	Molded plastic	Extruded plastic	Film	Laminates	Tires	Rubber specialties	Fibers	Adhesives and coatings	Polymer additives
A, C-1	• •	• •	• •	•			•	•	
B, D, K	• •	• •	• •				• •		
C-2									
E, F	• •	• •	•	•				•	•
G	•	•	• •					•	
H									
J								•	•
L					•	• •		•	
M						• •			
N, P, Q			•		•	• •		•	•

* See Table 13-3 for code.

TABLE 13-5
The ABS Polymers



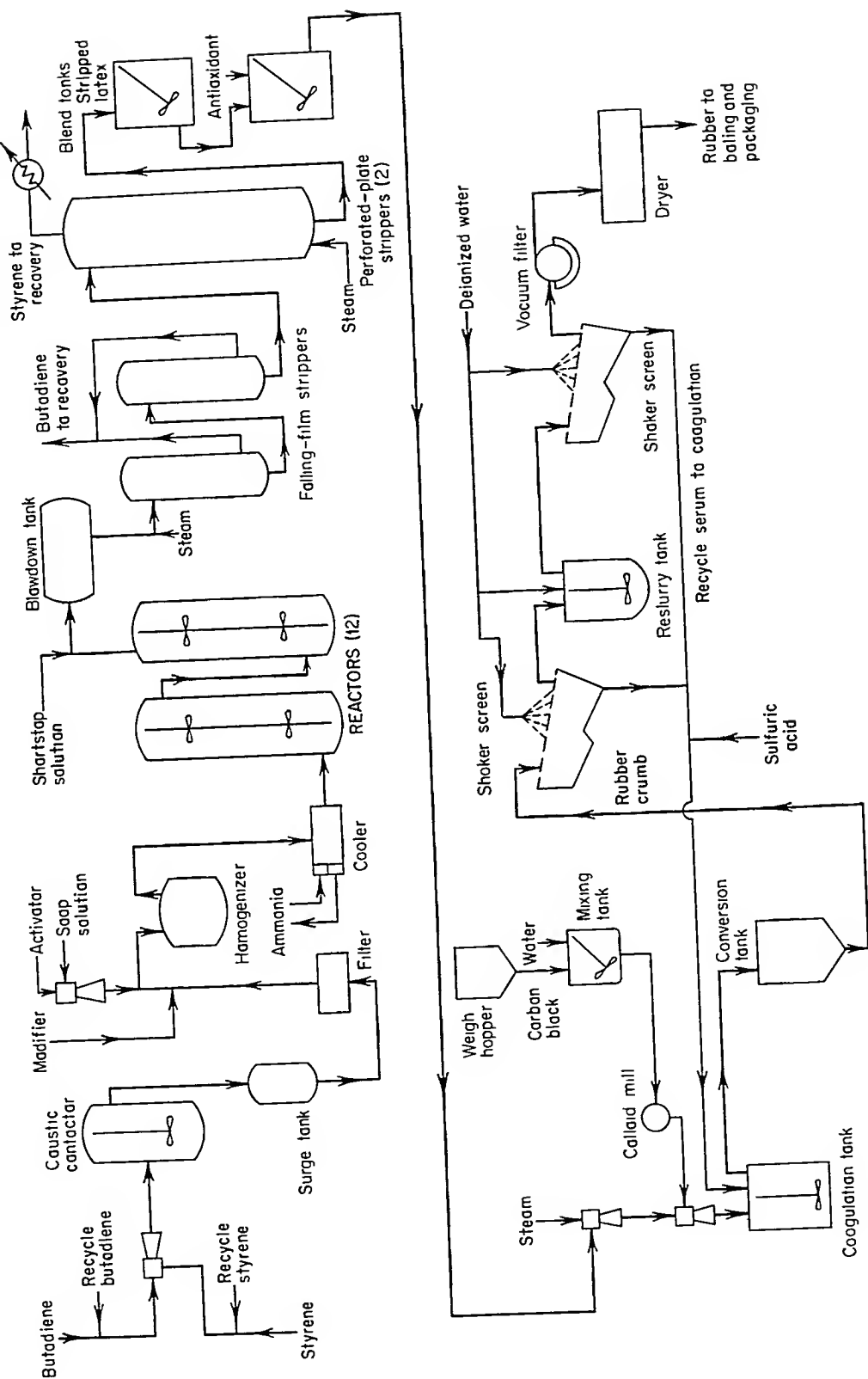


FIGURE 13-7
Continuous process for styrene-butadiene rubber production [8].

quently, a feed concentration of about 30% styrene is used to achieve a 25% styrene polymer. About 70% of the SBR rubber goes to make tires in which carbon black will be used as a reinforcement and oil as an extender-plasticizer. Most producers sell SBR as master batches that have been compounded before coagulation. Common loadings are 37.5 or 50 parts of oil per 100 of rubber and 40 to 75 parts of carbon black per 100 of rubber. The SBR production in 1973 breaks down as follows:

Polymer type	Polymer weight*	Total weight*
Cold SBR:		
Not master-batched	0.33	0.33
Oil master-batched	0.44	0.63
Black master-batched	0.02	0.03
Oil + black master-batched	0.21	0.45
Hot SBR:		
Not master-batched	0.21	0.21
Total	1.21	1.65

* $\text{kg} \times 10^{-9}$; Source: Bureau of the Census, Washington, D.C.

Latex paints are based on the stripped latex together with suitable pigments, stabilizers, and other additives. Higher styrene contents give somewhat better abrasion resistance (from a higher T_g), and conversions may be run almost to completion (with high molecular weights and branching), since film formation does not involve much polymer flow. Some latexes are intentionally cross-linked by copolymerizing a tetra-functional monomer, divinyl benzene. These gelled latex particles act like organic fillers and are used to smooth out extrusion of linear rubber. The random copolymer produced by a coordination complex catalyst in solution, "stereo SBR," has many of the same properties as the free-radical material. It probably contains less branching and less 1,2-polymerization of the butadiene. On the other hand, block copolymers produced by rhythmic alternation of styrene and butadiene in the feed of a Ziegler polymerization are quite different in mechanical behavior from conventional SBR (see Sec. 4-5, Coordination-Complex Systems).

Copolymerization of acrylonitrile with butadiene is usually carried out in free-radical emulsion polymerization with high conversion. Because so many modifications are marketed (for example, low, medium, and high nitrile content) and the total volume is smaller than SBR, production is most often batchwise rather than continuous. The outstanding property of NBR, or *nitrile* rubber, as it is called, is resistance to swelling in nonpolar solvents. With increasing acrylonitrile content, the cohesive energy density increases, so swelling in nonpolar, low-cohesive-energy-density solvents decreases (Sec. 2-5). The term "solvent-resistant rubber" is used, but it should be regarded cautiously because a polar rubber actually swells more than a nonpolar one in a polar solvent.

In the 1970s a new family of polymers became available based on a 1:5 mole ratio of acrylonitrile to butadiene [9]. These liquid polymers (mol wt of 3000 to 4000) are made with a variety of end-groups. Carboxyl, amine, and vinyl groups allow a choice of subsequent reactions. The carboxyl and amine groups react with epoxies

and can be part of castings or adhesives. A vinyl group at each end makes the "pre-polymer" capable of chain polymerization with a functionality of four (or more, if the original polymer is branched). A casting compound is illustrated in Table 13-6. The classification is complex from the standpoint that the butadiene and acrylonitrile presumably form a random copolymer, which is then block-copolymerized with the styrene. Thus the result is part random, part block, an interesting hybrid.

The atactic homopolymer of styrene is produced by free-radical initiation in bulk or suspension polymerization. Few details of commercial bulk polymerization have been made public. A two-stage scheme is shown in Fig. 13-8. A peroxide (or a controlled amount of oxygen) might be added to obtain the low conversion in stirred stainless-steel reactors over a period of 10 to 30 h. Final polymerization to high conversion is obtained in a tower with a temperature that rises from 100 to 200°C. A scraper could be used to help move the polymer. Finally a vented extruder simultaneously removes unreacted monomer and forms the product into molding pellets. Suspension polymerization (Fig. 13-9) in a batch process might require 8 to 12 h at 70 to 100°C. Coagulation is not necessary, since the particles are large enough to be filtered out directly after steam treatment to remove unreacted monomer. Suspension polymerization also is ideal for producing the cross-linked beads required for ion-exchange resins. In the presence of about 10% divinyl benzene, the monomer beads are gelled at a low conversion, triggering the Trommsdorff effect (Sec. 5-1). This cuts the time for almost 100% conversion down to about $2\frac{1}{2}$ h. From the 1000-gallon, glass-lined reactors (Fig. 13-10), the beads (0.30 to 1 mm diameter) are transferred after washing and drying to separate kettles, where they are reacted with sulfuric acid or chloromethyl ether followed by trimethylamine, making a quaternary ammonium group. A weak anion-exchange group results if dimethyl amine is used instead.

TABLE 13-6
Formulation and Properties for Vinyl-terminated
Butadiene-Acrylonitrile Casting [9]

Component	Parts by weight
Hycar VTBN (B.F. Goodrich Chemical Co.)	50
Styrene	50
Dimethylaniline	0.2
Benzoyl peroxide	2.5
TiO ₂	20
Stir together at 27°C, cast and hold at 27°C overnight followed by 10 min at 120°C.	
Property	Value
Tensile strength	8.2 MPa (1210 psi)
Elongation	320%
Stress at 100% elongation	1.2 MPa (170 psi)
Hardness (Shore A)	39

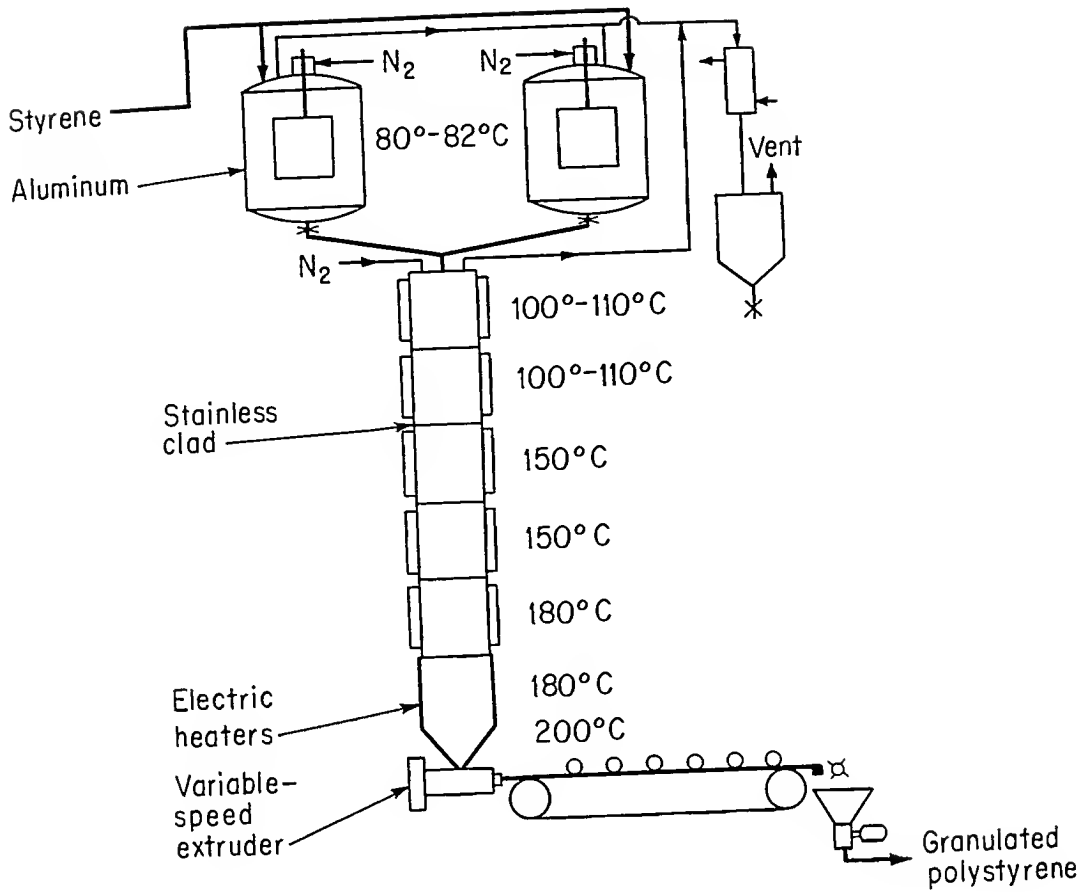


FIGURE 13-8
Continuous polymerization of styrene [10].

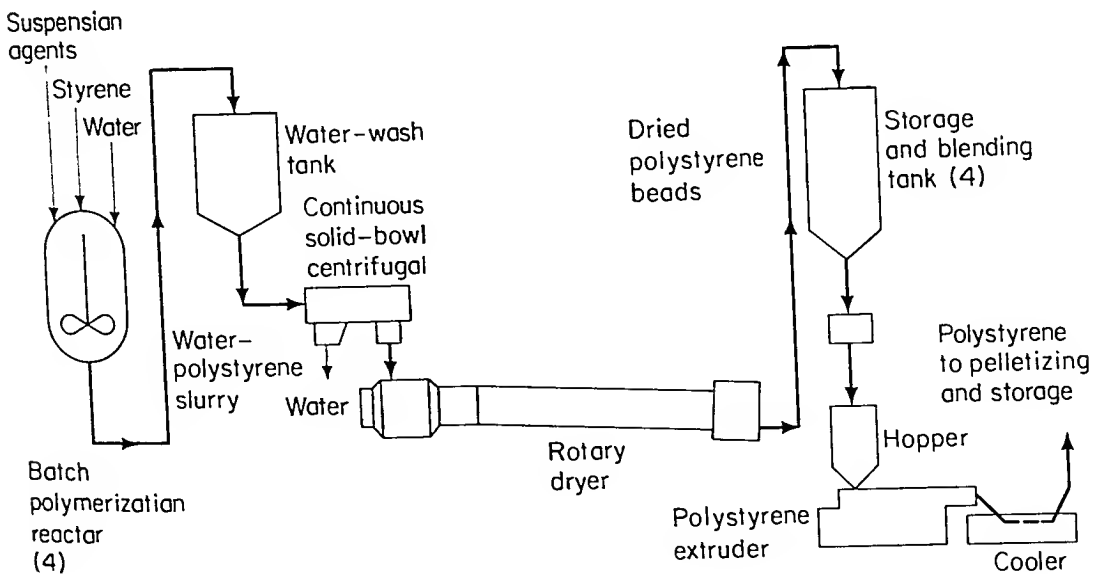


FIGURE 13-9
Suspension polymerization of styrene [11].

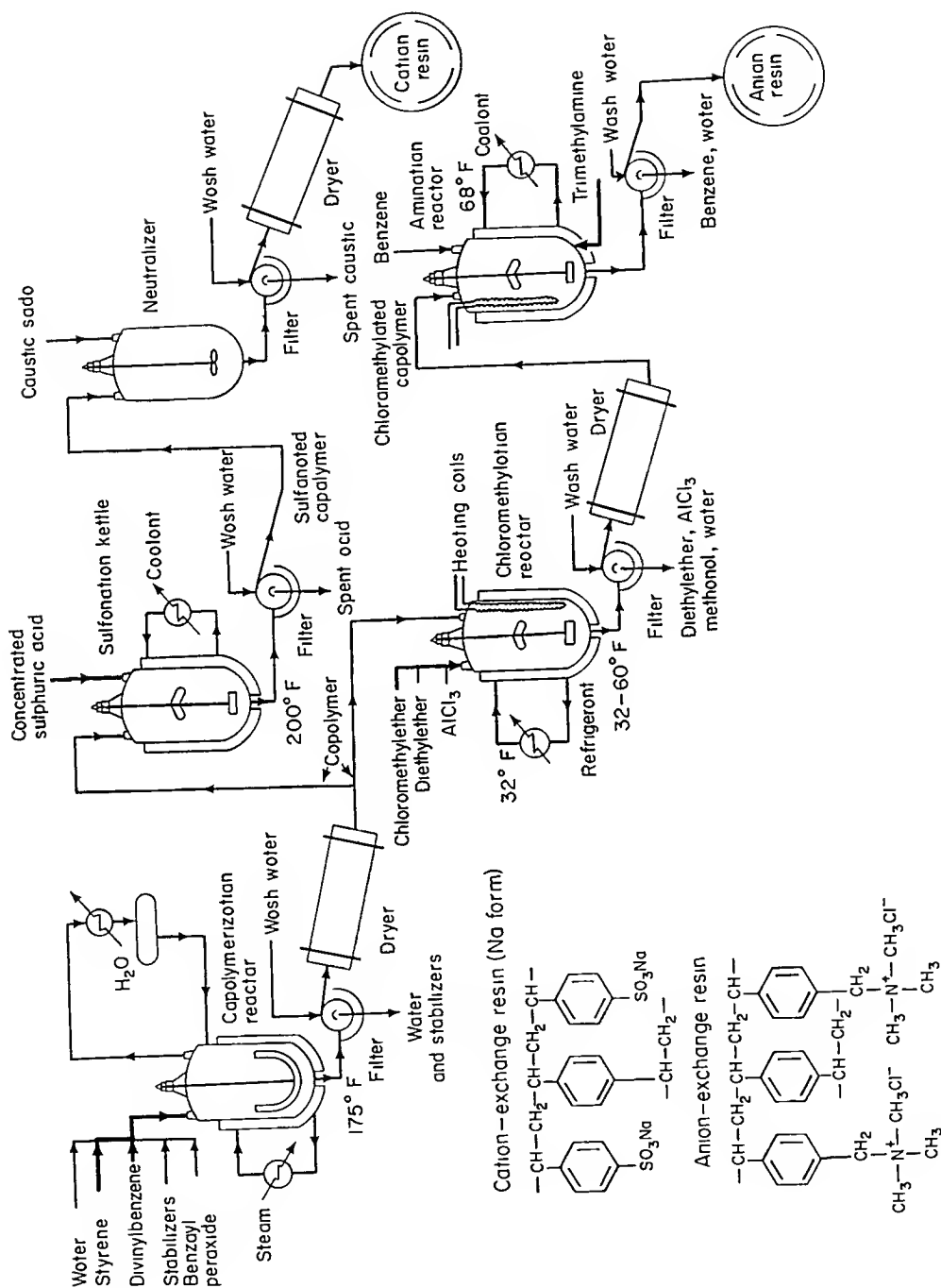
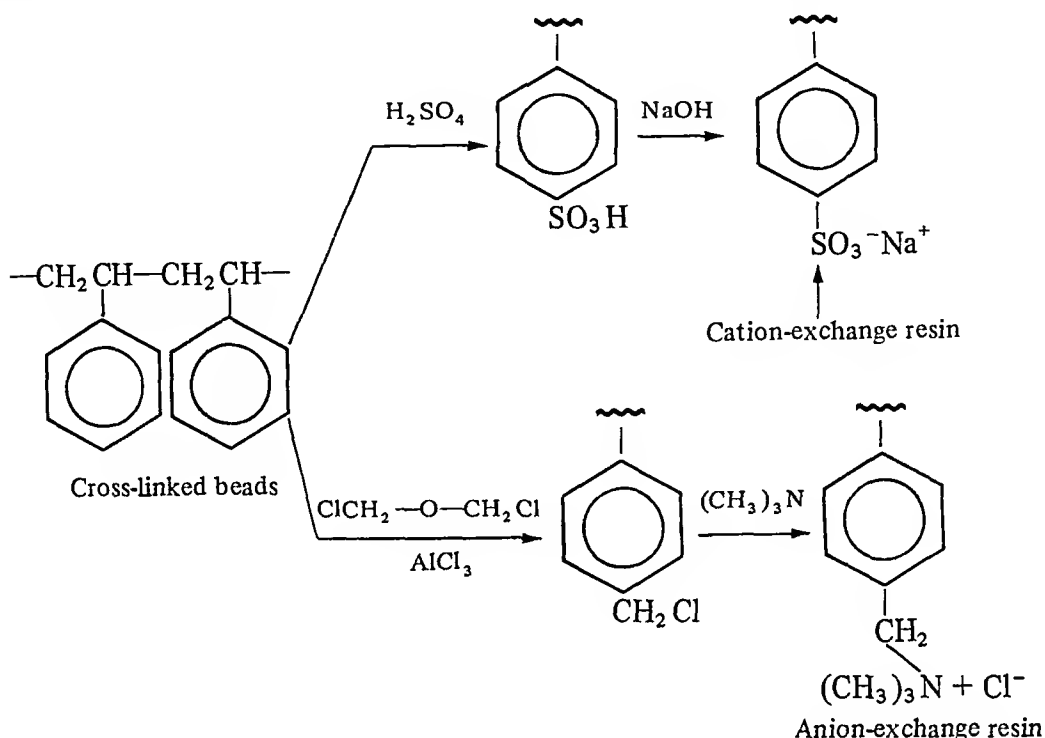


FIGURE 13-10
Ion-exchange resins based on polystyrene beads [12].

For applications that require the crystal clarity of polystyrene, but where the chemical resistance and tensile strength are marginal, a copolymer of styrene with acrylonitrile is available (SAN). Some grades will bear more than twice the stress that conventional polystyrene does before crazing or cracking. Where clarity is not needed,



polystyrene can be toughened by mechanically blending it with a rubbery polymer. Originally blends were made by milling polystyrene with SBR rubber on a hot mill or by coagulating latexes of the two ingredients together. Recently the practice has been to dissolve SBR or polybutadiene rubber in styrene monomer and then polymerize in bulk. This results in some grafting along with homopolymerization. In these rubber-modified resins, maximum toughness is achieved by selecting the two components so that they are compatible enough to wet each other well but incompatible to the extent that the rubber will be present as discrete droplets about 0.005 cm in diameter within a continuous polystyrene matrix. The impact strength can be raised to over 1 ft-lb/in (53 J/m) of notch from the unmodified value of 0.3 by a rubber content of 10%.

The combination of all three monomers is different enough to result in a separate class of materials, the ABS resins. Simultaneous terpolymerization does not give the desired heterogeneity that goes along with high impact strength and general toughness. The two processes favored are a blending of latexes of styrene-acrylonitrile and acrylonitrile-butadiene copolymers or a grafting of styrene and acrylonitrile on a polybutadiene backbone in latex form. In the blending process (Fig. 13-11) the butadiene-acrylonitrile copolymerization usually is short-stopped at about 75% conversion and residual monomer is stripped before blending. The styrene-acrylonitrile copolymerization can be carried substantially to completion, as can the grafting of the two monomers on a polybutadiene latex. Typical recipes include, in each case, surfactants, a water-soluble peroxide, and a chain transfer agent (mercaptan) (Table 13-7).

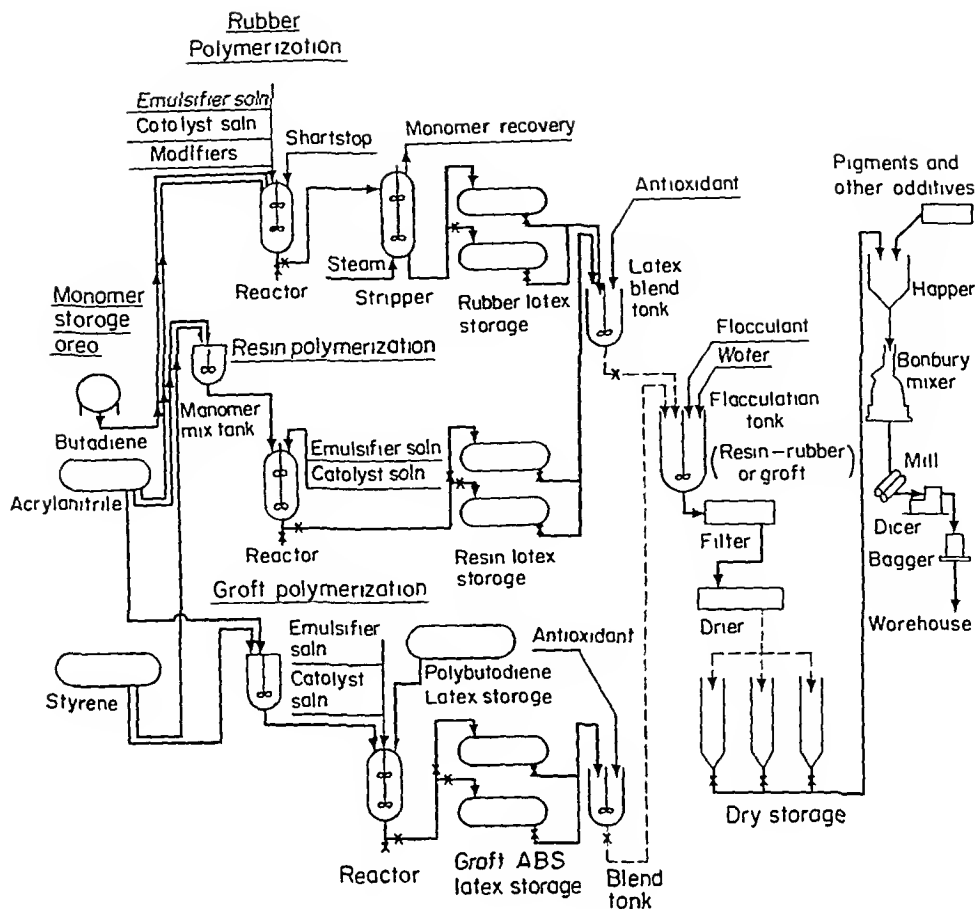


FIGURE 13-11

Flow scheme for ABS resin production by two routes [13]. (From *Manufacture of Plastics*, by W Mayo Smith, copyright 1964 by Reinhold Publishing Corp., by permission of Van Nostrand Reinhold Company.)

TABLE 13-7

Typical Polymerization Recipes for ABS Components (Parts by Weight) [13]

	Rubber	Resin	Graft
Water	180	200	200
Butadiene	65		
Styrene	—	70	42
Acrylonitrile	35	30	24
Rubber latex (solids)	—	—	34
Sodium cetyl sulfate	3.0		—
Sodium alkyl aryl sulfonate	—	2.0	
Sodium disproportionated rosin	—	—	2.0
Cumene hydroperoxide	0.2	—	—
Potassium persulfate	—	0.30	0.2
Sodium bisulfite	—	0.01	
Mercaptans (C ₁₂)	1.0	0.35	1.0
Time	17 h	4 h	Not given
Temperature	41°C	50°C	50°C
Conversion	75%	100%	100%

The three monomers representing glassiness (styrene), rubberiness (butadiene), and polarity (acrylonitrile), can be placed at the corners of a triangular composition diagram (Fig. 13-12). Even the triangular diagram is not enough to catalog all the significant variations that are possible. Neither steric variations (tacticity and cis,trans isomerism) nor cross-linking are shown. As indicated previously, both random and block copolymers of styrene and butadiene have the same ratio of monomers, but they differ in properties. On the diagram the "barrier" resins, which appear at high acrylonitrile content, are so called because of their low permeability to oxygen and carbon dioxide. Functional groups affect permeability strongly (Table 13-8). This is reflected in the series of styrene-acrylonitrile copolymers (Table 13-9). Such polymers are used as margarine tubs and vegetable oil bottles. For some time, copolymer bottles were tested as soft-drink containers, for which the low permeability was a great asset. However, they were eventually withdrawn from the market because unreacted acrylonitrile (a suspected carcinogen) might be extracted by the contents. Polymerized or copolymerized acrylonitrile does not pose a health threat.

Even more complex are compositions that are physical mixtures of polymers. One important outlet for ABS resins is in blends (*alloys*) with poly(vinyl chloride). In Europe rigid poly(vinyl chloride) is used for many sheet-forming applications such as door liners and crash pads. In the United States ABS has been used. It would appear that alloys may be developed that combine the flame retardancy inherent in poly(vinyl chloride) together with the toughness and ease of fabrication of ABS.

Fibers bearing the generic name *acrylic fiber* contain at least 85% acrylonitrile. *Modacrylics* contain 35 to 85% acrylonitrile. Most familiar to the consumer by trade-marked names such as Orlon, Acrilan, Creslan, and Dynel, these fibers appear in rugs, upholstery, and apparel. Acrylonitrile may be solution-polymerized in water from which the polymer precipitates or in a polar solvent such as acetonitrile. Varying amounts of comonomers are used to modify mechanical properties or to facilitate the dyeing of products. In spinning fibers from solution, a wet technique may be used with a water-miscible solvent spun into a water bath. Dry spinning with evaporation of solvent is another possibility.

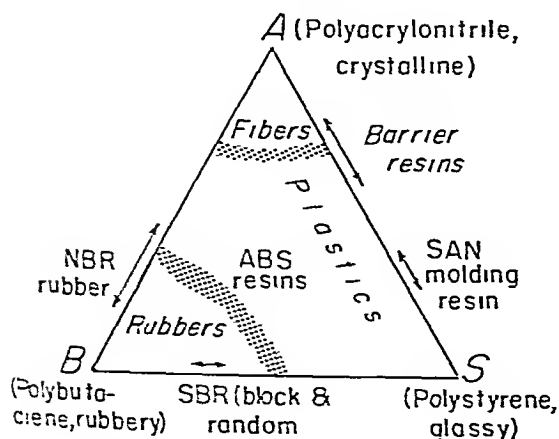


FIGURE 13-12

ABS compositions. Besides the homopolymers, interpolymers of the three building blocks give rise to numerous modifications. Locations indicated are only approximate.

TABLE 13-8
Effect of Functional Groups on Permeability* [14]

R group in $(-\text{CH}_2\text{CHR}-)$	Permeability to oxygen
$-\text{OH}$ (dry)	0.002
$-\text{CN}$	0.035
$-\text{Cl}$	8.02
$-\text{F}$	15.0
$-\text{CH}_3$	150
$-\text{C}_6\text{H}_5$	416
$-\text{H}$	501

*Permeability is in units of cm^3/day for an area of 100 in^2 and a driving force of 1 atm over a thickness of 0.001 in .

Use Pattern

Each of the members of the ABS group can be regarded as primarily a thermoplastics molding resin, as a rubber, or as a fiber (Table 13-10). An exception is the divinylbenzene-styrene copolymer, which is the basis for ion-exchange resins. This copolymer does not fit the three aforementioned end use categories because it is cross-linked and glassy. The *cast polyesters* in which styrene monomer is polymerized in the presence of an unsaturated polymer are discussed later on in the section on polyesters. Styrene also finds use in the coatings industry as a modifier for other resins. Styrenated alkyds and oils are uses that undoubtedly make use of grafting to some extent. However, the heavyweight of the ABS group in the coatings business is the high-styrene SBR latex. The interior water-based paints introduced right after World War II were made from SBR latexes. The vinyl and acrylic latexes now dominate that market.

13-4 THE DIENE POLYMERS

Although conjugated diene monomers are capable of exhibiting a functionality of four in polymerization reactions, the important examples are linear or branched polymers

TABLE 13-9
Gas Permeability* of Acrylonitrile-Styrene Copolymers [14]

Weight % acrylonitrile in copolymer	Permeability to oxygen	Permeability to carbon dioxide
0	416	1250
25	66.8	217
60	4.5	7.5
67	2.3	5.3
82	0.25	0.83
100	0.035	0.15

*Permeability is in units of cm^3/day for an area of 100 in^2 and a driving force of 1 atm over a thickness of 0.001 in .

TABLE 13-10
End-Use Pattern for the ABS Group of Polymers

Polymer*	Molded plastic	Extruded plastic	Film	Laminates	Tires	Rubber specialties	Fibers	Adhesives and coatings	Polymer additives
A, G, J	• •	•	•					•	
B					• •	•		•	•
C							• •		
D						• •		•	•
E						• •			
F-1, F-3					• •	• •		•	•
F-2								• •	•
F-4						•			• •
H (ion-exchange)									
K, L	• •	• •	•	• •				•	•
M	•			• •				•	

*See Table 13-5 for code.

with residual unsaturation (Table 13-11). Natural rubber (*cis*-1,4-polyisoprene) was harvested and used in the Western Hemisphere for centuries before it was introduced to Europe over two hundred years ago. Because of the remoteness of the tropical climates where rubber could be grown, Germany in World War I and Germany, Russia, and the United States in World War II intensified research on duplicating the natural product on which so much of their transportation depended. Substitutes such as the SBR rubber were found, but synthesis of the stereoregular polymer was not accomplished until the 1950s and 1960s. There was no rush to put synthetic "natural" rubber into production, however, because by this time the "substitutes" had come to be appreciated for their own properties.

Natural rubber is recovered as a latex by tapping trees. Although the process resembles maple sugar tapping, the latex is carried in a separate layer from the sap of the rubber tree. The latex contains about 35% rubber and another 5% of solids comprised of proteins, sugars, resins, and salts. Most tree latex is coagulated and formed into sheets 3 or 4 mm thick. At one time, smoking (exposure to fumes from burning wood) was favored as a method of preserving against mold and bacterial attack. The same process is used for curing hams and fish. Nowadays, other types of fungicides and bactericides can be used with air-dried sheets. While there are many standard grades of natural rubber, names frequently encountered are "ribbed smoked sheets," and "pale crepes."

Since the middle 1970s, attempts to recover *cis*-polyisoprene from guayule have received the support of U.S. and Mexican governments [15]. Guayule is a shrub native to the southwestern United States and northern Mexico. Unlike the rubber tree, which is tapped again and again using a sizable input of hand labor, the guayule shrub is harvested in its entirety. The process can be automated. Besides the 20% by weight of rubber that can be extracted with solvents, dried guayule has another 20% of resin and wax that may have commercial value. Two major incentives for develop-

TABLE 13-11

The Dienes (Butadiene included in Table 13-5)

A

CH₃

Isoprene, CH₂=C(CH₃)—CH=CH₂ (*T_b* = 34°C)

1. (cis) Tree latex, trapped from *Hevea brasiliensis*; *T_g* = −73°C, *T_m* = 28°C; very low crystallinity; "natural rubber, NR rubber"
2. (cis) Coordination complex solution polymerization; *T_g*, *T_m* same as 1; "IR rubber"
3. (trans) Tree latex; *T_g* = −73°C, *T_m* = 74°C; medium crystallinity; "balata, gutta-percha"
4. (trans) Coordination complex solution polymerization; *T_g*, *T_m* same as 3; "synthetic balata"

B

Cl

Chloroprene, CH₂=C(Cl)—CH=CH₂ (*T_b* = 59°C); free-radical, emulsion polymerization; *T_g* = −50°C, *T_m* = 80°C; low crystallinity, especially when crosslinked; "CR rubber, Neoprene"

F

Polymer *A*-1 heated in solution with catalyst to make "cyclized rubber"

G

Polymer *A*-1 + Cl₂ (about 65 wt % Cl₂ in product); made in CCl₄ solution; *T_g* > 50°C; "chlorinated rubber"

H

Polymer *A*-1 + styrene or methyl methacrylate; graft copolymerization on polymer in latex; "Hcveaplus"

C

Norbornene, C₇H₁₀ (*T_b* = 96°C); ring scission polymerization; *T_g* = 35°C

D

Cyclopentene, C₅H₈ (*T_b* = 44°C); ring scission polymerization

1. (cis) *T_g* = −114°C, *T_m* = −41°C, polypentenamer
2. (trans) *T_g* = −97°C, *T_m* = −97°C, polypentenamer

E

Acetylene, CH≡CH (*T_b* = −84°C); conductive polymer

T_b = boiling temperature

T_g = glass transition temperature

T_s = softening temperature

T_m = melting temperature

T_b = boiling temperature
 T_g = glass transition temperature
 T_s = softening temperature
 T_m = melting temperature

ment of guayule are the goal of independence from an overseas source of raw materials as far as the Americas are concerned and the productive use of arid and semiarid lands in the United States and Mexico.

The naturally occurring *trans*-1,4-polyisoprene is recovered as a latex from trees also. Gutta-percha and balata are obtained from trees in southeast Asia and South America, respectively. The unvulcanized material crystallizes enough to be quite dimensionally stable at room temperature. It may have been the first thermoplastic resin, since it was used as an electrical insulation for submarine cable in England and Germany [16] as long ago as 1848. A major application today for the vulcanized gutta, golf-ball covers, indicates the typical properties of the polymer. Another novel application is as a splint in orthopedics [17]. The synthetic *trans*-1,4-polyisoprene made with Ziegler catalysts is preferred. Direct molding is used to customize the splint. When heated to 70 or 80°C, the polymer becomes amorphous and a sheet can be handled and shaped quite easily. It can be held against the skin where it becomes dimensionally stable after a few minutes due to crystallization. It can replace plaster of paris, which is the older material used for this purpose. The polymer has the advantages of being light, durable, attractive, and unaffected by water.

The remarkable degree of control over structure in diene polymers is illustrated in Table 13-12. These values are selected from among hundreds found in the literature. A commercially successful catalyst system may use similar systems, but economic considerations will modify the requirements. Predominantly *cis* polymers have the largest market, although the *trans* polymers are available. The major differences between isoprene or butadiene polymerization by the Ziegler process and the process described for ethylene and propylene (Sec. 13-2) are that the reaction may be short-stopped at 80 to 90% conversion, that monomers are less volatile and somewhat more difficult to recover, and that the polymer remains soluble in the medium and must be precipitated by adding a diluent. In one process (Fig. 13-13) a modified Ziegler catalyst (aluminum, cobalt) in benzene is charged together with butadiene to the first in a line of cooled, agitated reactors. In 4 to 6 h total residence time at 20 to 50°C, conversion reaches 80 to 90% and is short-stopped, presumably by an alcohol or some other reactive material. Just before short-stopping, an additional catalyst may

TABLE 13-12
Structure of Polymers from Conjugated Dienes [18]

Monomer	Initiator	Polymer structure, %			
		<i>cis</i> -1,4	<i>trans</i> -1,4	1-2	3-4
Butadiene	Free radical, 50°C	19	60	21	
	Butyl lithium-hexane, 20°C	33	55	12	
	Cobalt chelate-AlEt ₂ Cl, Al/Co = 5:20	99	1		
Isoprene	TiCl ₄ -AlR ₃ , Al/Ti < 1	6	91	3	
	Free radical, 50°C	18	75	5	5
	Butyl lithium-pentane	93	—	—	7
	TiCl ₄ -AlEt ₃ , Al/Ti > 1	96	—	—	4
	TiCl ₄ -AlEt ₃ , Al/Ti < 1	—	95	—	5

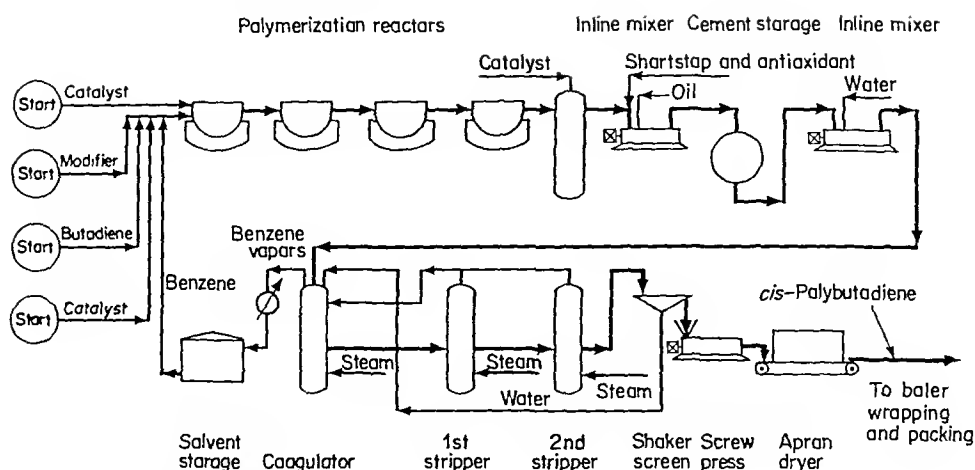
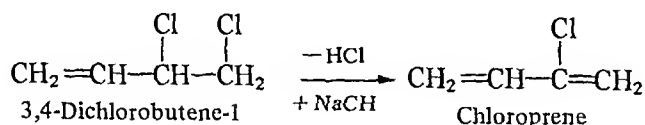


FIGURE 13-13

Butadiene polymerization [19].

be added to make a molecular weight "jump," probably involving a dimerization. This is a useful device for achieving the high molecular weight needed for oil-extended rubber. Since the jump occurs at high conversion, only the final cement or dope has a high viscosity. An efficient solvent-recovery system is essential for economic operation.

The emulsion polymerization of chloroprene by free-radical initiation dates back to the early 1930s. While the *trans*-1,4 structure predominates, it is not all head-to-tail, and there is some branching. Most chloroprene is made by chlorination of butadiene followed by isomerization to give 3,4-dichlorobutene-1. Then hydrogen chloride is removed by aqueous sodium hydroxide [20].



Some monomer may still be made by an older process in which hydrogen chloride is added to vinylacetylene. The continuous emulsion polymerization uses a series of stirred reactors similar to SBR production, although only one is shown in Fig. 13-14. A typical residence time is 2 h for 70% conversion at 40°C. Some grades are produced in batch reactors and conversions can range up to 90% [21]. Sulfur or sulfur compounds are included possibly as antioxidants or as chain transfer agents. Several of the commercial rubbers probably have small amounts of comonomer such as styrene, acrylonitrile, or 2,3-dichloro-1,3-butadiene. Some latex is used directly for dipped goods and paints, but most of it is coagulated. The coagulation differs from the method used for SBR in that after neutralizing the emulsifier with acetic acid, the unstable latex is coagulated on the surface of a chilled, rotating drum. The strong film of polymer which forms rapidly can be pulled off the drum continuously, and washed and dried in film form before being gathered into a rope which is chopped into short pieces for packaging. The unvulcanized rubber crystallizes sufficiently to appear hard

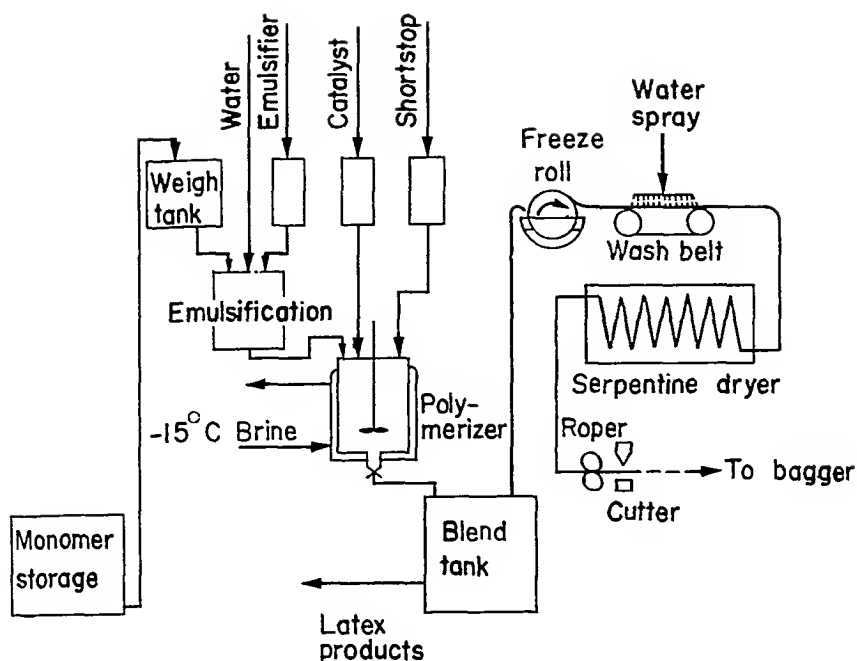
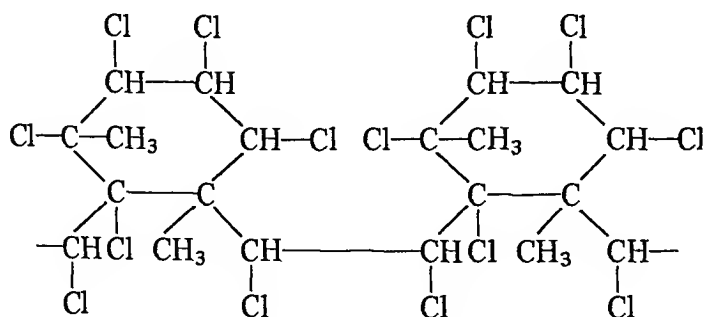


FIGURE 13-14

Schematic flowsheet for the polymerization and isolation of polychloroprene [21].

and horny with little tendency to flow. Cross-linking can be carried out by heating with 5 parts ZnO and 4 parts MgO per 100 parts of rubber. As with any rubber, many other vulcanizing combinations are used.

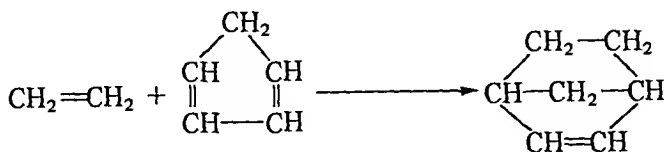
Two derivatives of natural rubber that have been produced for many years are cyclized rubber and chlorinated rubber. The first of these may be produced in solution by heating with a strong acid such as H_2SnCl_6 . The structure that results resembles a ladder to some extent (Sec. 11-3). It is still quite soluble and finds use in adhesives and coatings. Chlorinated rubber with about 65% chlorine in the product has been used as a coating for many years. One particular application is in traffic paints (actually lacquers). The chlorinated rubber is a good binder for the pigments and has excellent abrasion resistance.



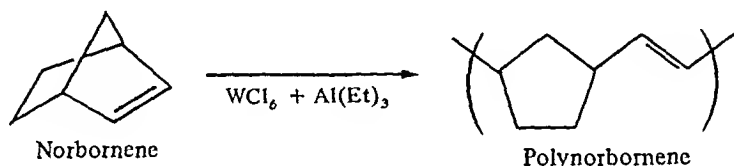
Chlorinated rubber [22]

The ring-scission polymerization of cyclopentene gives a product very similar to the diene polymers, in that one unsaturation remains in the main chain for each monomer unit introduced (see Sec. 4-7). Although a considerable literature [23, 24, 25] exists on polypentenamers, neither the cis nor the trans polymer has achieved

widespread commercial use. On the other hand, a related rubber was introduced in 1976 in France and has since been offered in other countries. The monomer is norbornene (1,3-cyclopentylenevinylene) made by the Diels-Alder condensation of ethylene with cyclopentadiene:

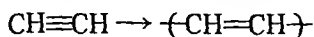


The ring-opening polymerization can be carried out by a variety of catalysts, for example, WCl_6 with aluminum triethyl (26).



There can be a considerable amount of cis configuration as well as the trans shown here. The commercial product is a high-molecular-weight (2×10^6) plastic with a T_g of 35°C . To be used as a rubber, plasticizing oils must be added to lower T_g . A fascinating feature of the material is its ability to absorb large amounts of oil and to remain a useful rubber. One mixing technique which can be used is dry-blending of polymer and plasticizer, a method widely used with poly(vinyl chloride). If the oil is added while the powdered polymer is tumbled, the final mixture remains a free-flowing powder which can be fed directly to an extruder. In a typical recipe (Table 13-13), the polymer is less than 20% of the final weight of the product. Some applications have been engine mounts, roll coverings, sealing materials, and tail-light gaskets for automobiles [27].

Polyacetylene is another polymer with residual chain unsaturation.



Catalytic polymerization of acetylene gas on a glass surface gives a lustrous, silvery film with a fair amount of mechanical strength [28]. The polycrystalline films (mainly trans isomer) can be "doped" with small amounts of AsF to give conductivities of over $100 (\text{ohm}\cdot\text{cm})^{-1}$. Control of electrical and magnetic properties could lead to applications in solar-cell technology [29].

Another important source of diene polymers is rubber reclaimed from used tires. Metal and fabric are separated from the tire before treatment with alkali which breaks down the sulfur cross-links. Reclaimed rubber from whole tires is mainly polyisoprene, polybutadiene, and styrene-butadiene rubber along with carbon black and other compounding ingredients.

TABLE 13-13
Compound Based on Polynorbornene (27)

Recipe	Parts by weight
Polynorbornene (Norsorex, American Cyanamid Company)	100
Zinc oxide	5
Stearic acid	1
Carbon black (HAF)	200
Aromatic oil	180
Paraffinic oil	20
Accelerator (<i>N</i> -cyclohexylbenzothiazole-2-sulfenamide)	5
Sulfur	1
Properties after molding 30 min at 150°C	
Tensile strength	20 MPa (2900 psi)
Elongation at break	320%
Hardness (Shore A)	55
Brittle temperature	-40°C

Use Pattern

The dienes enter into all the typical applications of natural rubber (Table 13-14). Tires consume about 70% of the *cis*-polyisoprene and butadiene. Polychloroprene, while not suited for tires because of heat buildup, is the most widely used oil-resistant rubber. It is much more resistant to oxidation at high temperatures than the hydrocarbon dienes or SBR. More than any other polymer, it merits the paradoxical encomium of being the general-purpose specialty rubber. The grafting of methyl methacrylate on natural rubber has been carried out on a commercial scale by polymerizing the monomer in a rubber latex. The primary use of the grafted material is as an additive to improve flow of unmodified rubber.

TABLE 13-14
End-Use Pattern for the Dienes

Polymer*	Molded plastic	Extruded plastic	Film	Laminates	Tires	Rubber specialties	Fibers	Adhesives and coatings	Polymer additives
A-1, A-2					• •	• •	•	•	
A-3, A-4						• •		•	
B						• •		•	
C (Foam)						•			
D									
E								• •	
F								• •	
						•			•

*See Table 13-11 for code.

13-5 THE VINYLs

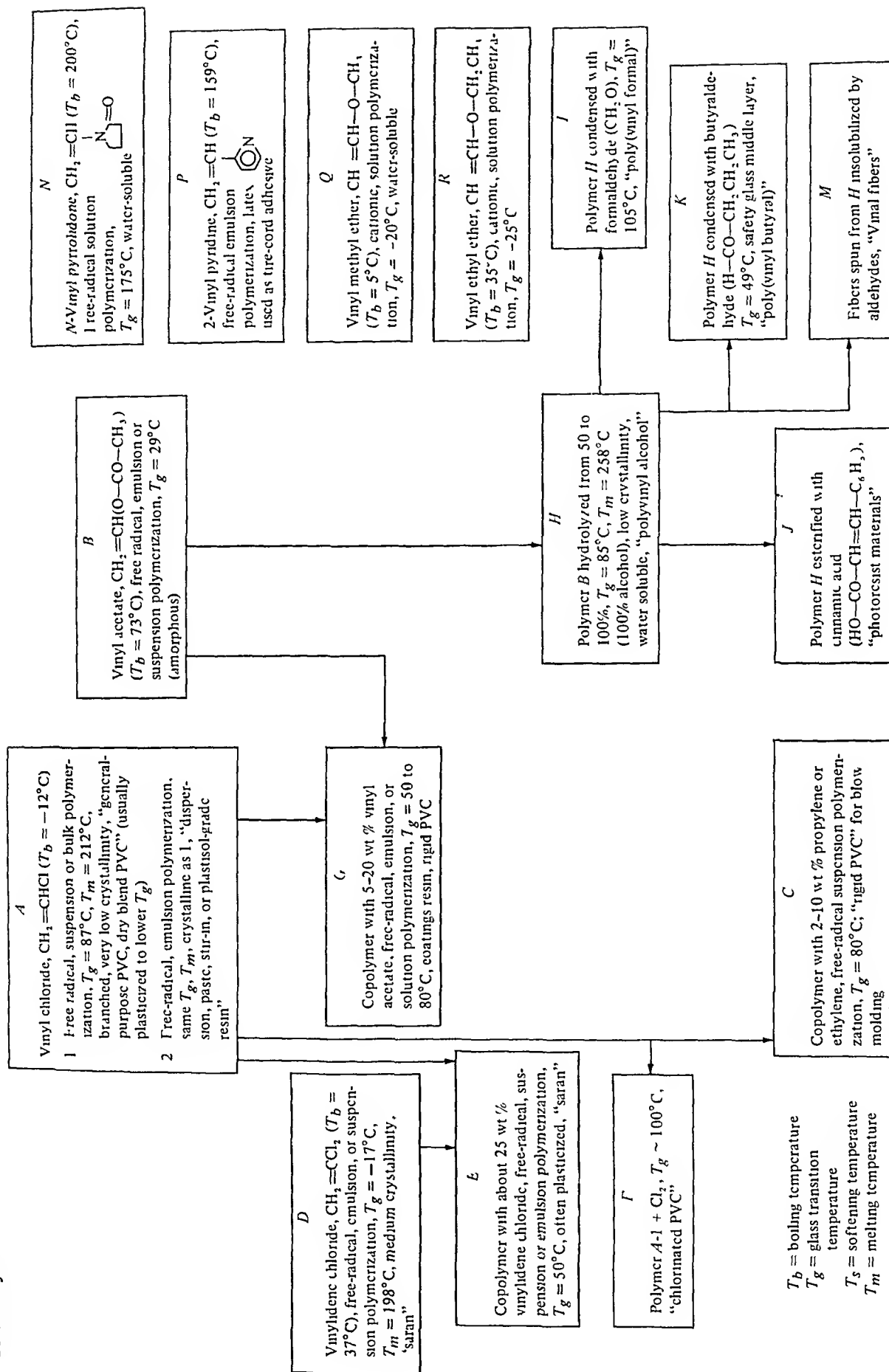
The group designated as vinyl polymers excludes vinyl benzene (styrene), vinyl cyanide (acrylonitrile), and vinyl fluoride (Table 13-15). The observation recorded by Regnault in 1838, that vinylidene chloride is converted by exposure to sunlight in a sealed glass tube to an insoluble polymer, often is cited as the beginning of polymer science. However, a hundred years passed before commercial use began. In the 1930s copolymers of vinyl acetate with a vinyl chloride were introduced. They are more soluble than the homopolymers of vinyl chloride and could be used in lacquers. The unique affinity of vinyl polymers for plasticizers was discovered at about the same time. No other thermoplastic matches the ability of poly(vinyl chloride) and its copolymers to form stable, dry, flexible solutions in nonvolatile liquids. Although triaryl phosphates and dialkyl phthalates dominate the plasticizer market today, thousands of liquids are marketed as plasticizers. As a generalization, one could say that every liquid with a volatility less than that of water at room temperature has been suggested as a vinyl plasticizer at one time or another. In Germany and the United States in the 1930s and 1940s homopolymers were developed using suspension and emulsion techniques that could yield useful plasticized items. Only in the last few years has there been much interest in a bulk process.

Until the introduction of exterior latex paints, most poly(vinyl acetate) was hydrolyzed to alcohol and reacted to form the butyral adhesive layer for laminating safety glass. The intermediate alcohol still has no single major market in the United States, but it is made into an important fiber in Japan.

Most vinyl chloride is polymerized by a suspension process. Jacketed, stirred reactors like the one in Fig. 13-15 vary in size from 2000 to 10,000 gal (8 to 40 m³). Individual reactors with volumes of 200 m³ have been made with bottom-entering agitators [31]. The charge to one of these "super-sized" reactors includes 100×10^3 kg of monomer. Reactors are stainless steel or glass-lined and must handle a pressure of about 1.5 MPa (220 psi). An initiator soluble in the monomer, such as lauroyl peroxide, is added to monomer, which is dispersed in about twice its weight of water containing 0.01 to 1% of a stabilizer such as poly(vinyl alcohol). Over a period of 8 to 15 h at 50 to 80°C, conversion may reach 80 to 90%. Polymer precipitates within the monomer droplets to form a reticulated structure. If the unreacted monomer is blown off at the end of the period by reducing the pressure, porous particles are obtained which can adsorb large volumes of plasticizer. *Dry-blend* resins are those which can adsorb 20 to 40 parts of plasticizer per 100 parts of polymer and still remain as free-flowing powders. Mixing and handling such systems is easier than operating with sticky, semifluid mixtures. The suspension polymer can be dried in rotary dryers, in spray dryers, or in combination grinding mill-classifier-dryers. Special suspension recipes are used with high conversion to give solid, nonporous resins. These are harder to dissolve in plasticizers. However, they are useful as additives in plastisols, since they do not increase the viscosity very much.

Dispersion (also called plastisol or stir-in) resins are made by emulsion polymerization in vessels similar to those used for suspension polymerization. The ease with which these polymers can be suspended in a plasticizer to give a free-flowing liquid is a result of the small particle size of the emulsion and the residual emulsifier. When the latex is spray-dried, most of the emulsifier remains on the surface of the particles

TABLE 13-15
The VinyIs



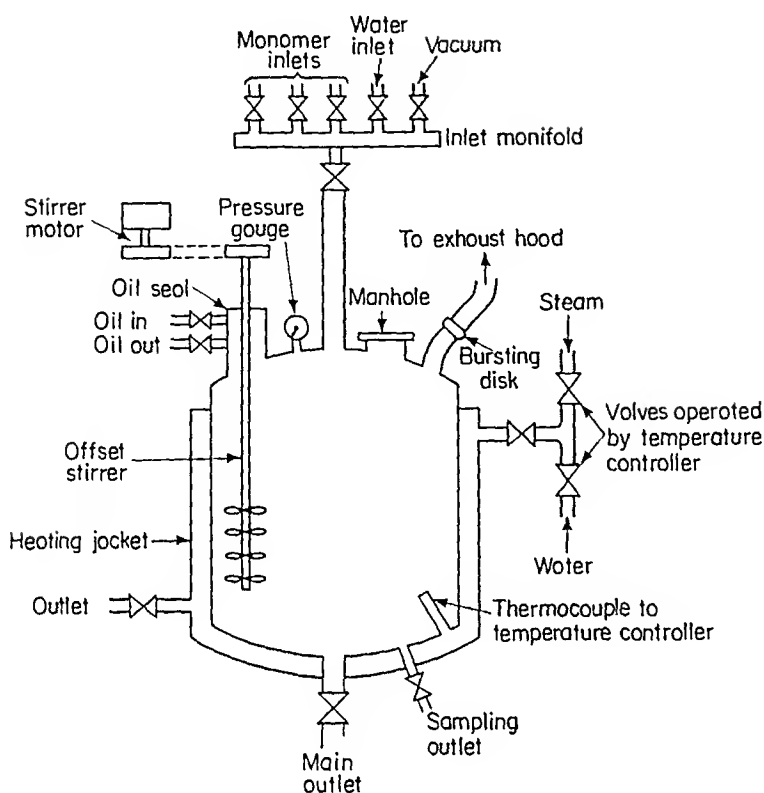


FIGURE 13-15

Typical polymerization vessel suitable for suspension or emulsion polymerization of vinyl chloride [30].

(actually aggregates of latex particles) and helps the plasticizer to wet them. Platisol molding was described in Sec. 12-6, and some effects of plasticization were described in Sec. 3-3.

Bulk polymerization has the advantage that no suspending or emulsifying agent is left in the resin to detract from optical clarity. A two-stage, batch process (Fig. 13-16) operates on a principle similar to that described for continuous polystyrene (Sec. 13-2). "Prepolymerization" in a stirred tank (0.016% azodiisobutyronitrile, 130 rpm, 62°C, 1 MPa) is carried to about 10% conversion. Further reaction to about 75% conversion occurs in a scraped-surface autoclave with slow agitation over a period of 10 or 12 h or more. Porous particles with diameters of 100 to 200 μm result after monomer is blown off and the polymer is recovered.

Copolymerization of vinyl chloride with vinyl acetate or vinylidene chloride gives polymers of lower T_g and better solubility. The main advantage of propylene copolymers is said to be stability and clarity in unplasticized, blow-molded bottles. Post-chlorination of poly(vinyl chloride) yields a material of higher T_g that has been recommended for pipes that can carry hot water without deforming.

The latexes that result from vinyl acetate polymerization have been used for exterior water-based paints. Emulsion polymerization can be carried to high conversion fairly rapidly. The rate is controlled by continuous addition of monomer. In one

process, 1 m³ of water containing 3% poly(vinyl alcohol) and 1% surfactant is heated up to 60°C [33]. Two streams, monomer and an aqueous persulfate solution, are fed in over a period of 4 or 5 h while the temperature rises to 70 or 80°C. Rate of addition is primarily limited by rate of heat removal. A final heating to 90°C may be used to react the last bit of monomer. When the latex is to be used as an adhesive, a plasticizer may be added. The popular white glues for paper and wood are poly(vinyl acetate) suspensions plasticized with liquids like castor oil.

Suspension polymerization is favored for poly(vinyl acetate) that is to be hydrolyzed to alcohol. A charge of 2000 kg of vinyl acetate containing 1.5 kg of benzoyl peroxide can be dispersed in 1 m³ of water containing 1 kg of poly(vinyl alcohol) [33]. In 6 to 8 h at 65 to 75°C (reflux), conversion is high enough that monomer can be steam-stripped out, the suspended beads can be hardened by cooling to 10°C, and the product can be filtered and dried.

Hydrolysis of the acetate can be carried out in concentrated methanol solution with a sodium methoxide catalyst. Various degrees of hydrolysis are marketed. The gelatinous poly(vinyl alcohol) precipitates as a slurry in the methanol. Some liquid is removed by expression (between steel rolls, for example) and the balance is taken

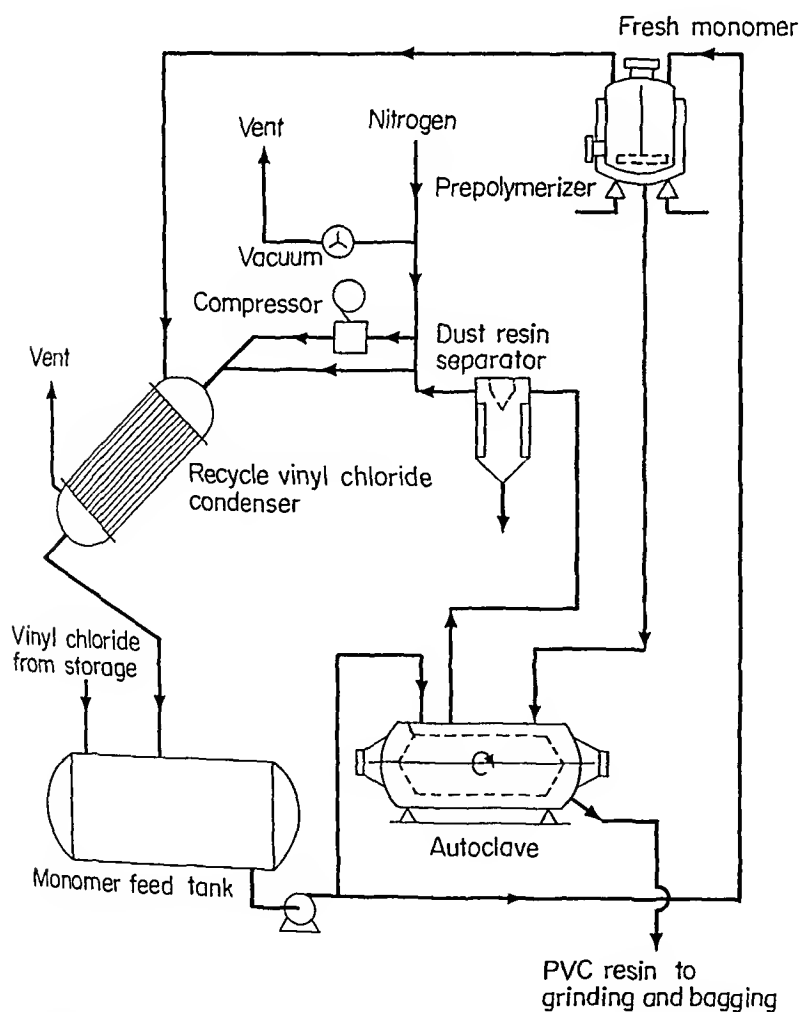
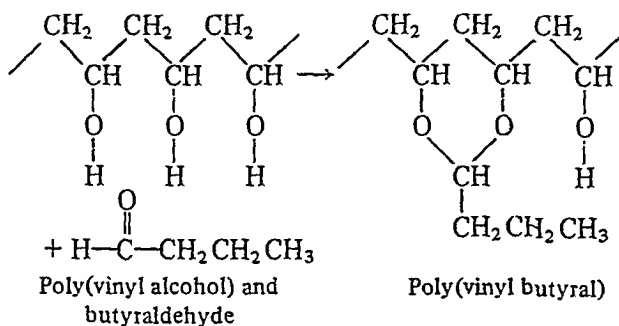


FIGURE 13-16
Continuous bulk polymerization of vinyl chloride [32].

off in a dryer. The product is ground to a fine powder for most applications. Poly(vinyl alcohol) is water-soluble and has been mentioned frequently as the stabilizing agent in many suspension polymerizations. All the other customary uses (thickening agent, gelling agent, cosmetic ingredient) of water-soluble polymers are conceivable for poly(vinyl alcohol). Fibers are produced in Japan by extruding a concentrated aqueous solution of poly(vinyl alcohol) into a sodium sulfate solution containing sulfuric acid and formaldehyde, which acts as a cross-linking agent.

When butyraldehyde is reacted with poly(vinyl alcohol) suspended in ethanol with sulfuric acid as a catalyst (5 to 6 h, 80°C), an intramolecular condensation is favored. If the reaction were irreversible, one would expect a great many isolated unreacted hydroxyl groups in the product. However, rearrangements do occur and the product may contain fewer than 10% unreacted OH groups rather than the theoretical limit of 13.5%.



Poly(vinyl formal) can be made by direct reaction of formaldehyde with poly(vinyl acetate) in aqueous sulfuric acid. The cyclic intramolecular structure is formed again.

Like poly(vinyl alcohol), an ester with pendant unsaturation cannot be made directly from the appropriate monomer. One such commercial polymer is produced by the reaction of cinnamoyl chloride with poly(vinyl alcohol) dispersed in pyridine [34]. A dry film of the product can be deposited from a solution and easily redissolved. However, when it is exposed to light, extensive cross-linking insolubilizes the film (Fig. 13-17). Lithographic plates are made by this photosensitive insolubilization.

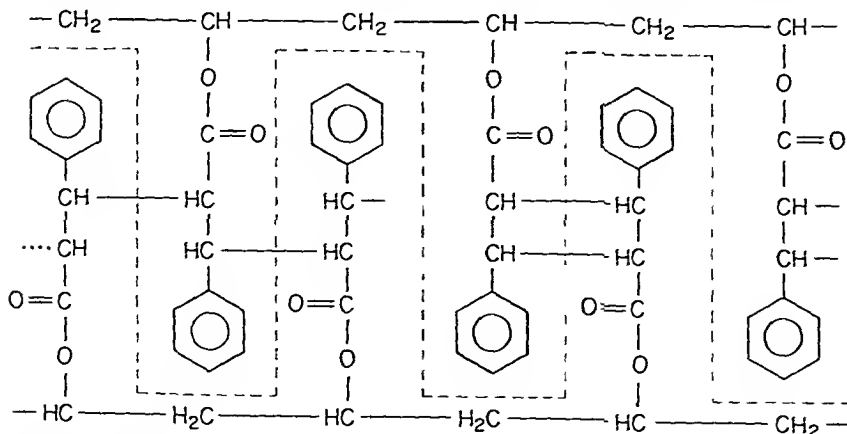


FIGURE 13-17
Cross-linked poly(vinyl cinnamate) [34].

TABLE 13-16
End-Use Pattern for the Vinyls

Polymer*	Molded plastic	Extruded plastic	Film	Laminates	Tires	Rubber specialties	Fibers	Adhesives and coatings	Polymer additives
A	• •	• •	• •	•				•	
B								• •	
C	• •								
D	•		• •				• •		
E								• •	
F		• •							
G	• •	•		•				• •	
H			•					• •	• •
J								• •	
K				•				• •	
L								• •	
M							• •		
N								•	•
P					•	•			
Q, R								•	

*See Table 13-15 for code.

Poly(vinyl alcohol) itself also can be photoinsolubilized in the presence of chromate ions and by exposure to much higher intensities of ultraviolet light than the cinnamate [34]. Photoresists are discussed also in Sec. 12-4, Coatings.

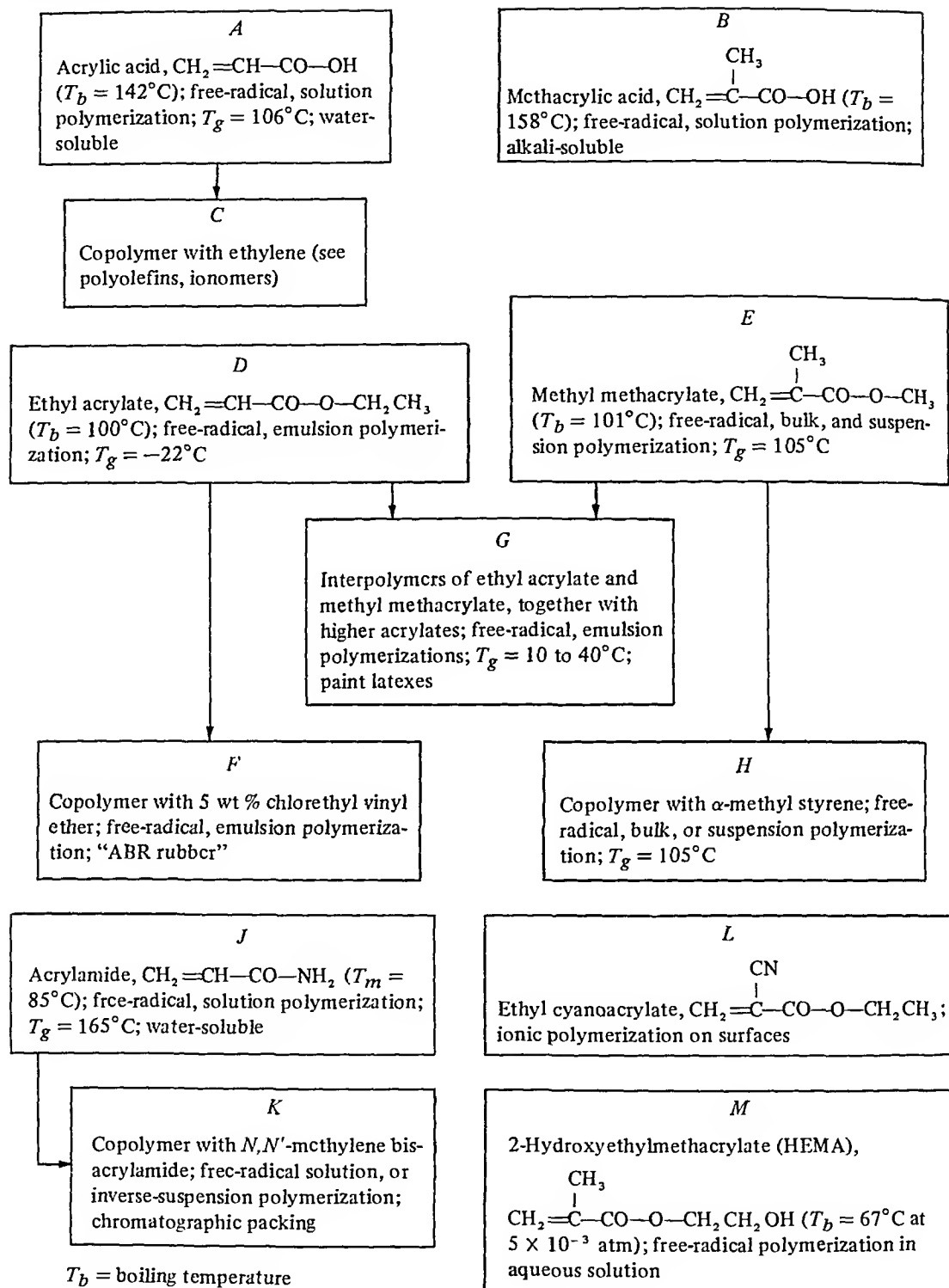
Use Pattern

Some familiar items made from plasticized poly(vinyl chloride) include garden hoses, laboratory tubing, and numerous film products such as shower curtains, diaper covers, and raincoats (Table 13-16). Blow-molded bottles from unplasticized vinyls have been commercially available for some time in Europe and the United States. Pipe and glazing are more common outlets for rigid vinyls. Although far outweighed by the chloride and acetate, several other vinyl monomers are homopolymerized industrially. Poly(vinyl ethyl ether) finds use in pressure-sensitive adhesives. Poly(vinyl pyrrolidone) (PVP) probably has its major market as a home-permanent wave-setting resin. It has unique complexing properties which make it valuable in some pharmaceutical and physiological applications. The iodine complex of PVP is an effective antiseptic much lower in toxicity than iodine itself. Also, about 7% PVP added to whole blood allows it to be frozen, stored at liquid-nitrogen temperatures for years, and thawed out without destroying blood cells.

13-6 THE ACRYLICS

Acrylic and methacrylic acid and their esters are included in the acrylic group (Table 13-17). Otto Röhm published his doctoral thesis dealing with acrylic compounds in 1901 in Germany. First in Germany (1927) and then in the United States (1931) he was associated with the commercialization of acrylic polymers as coating resins.

TABLE 13-17
The Acrylics



T_b = boiling temperature

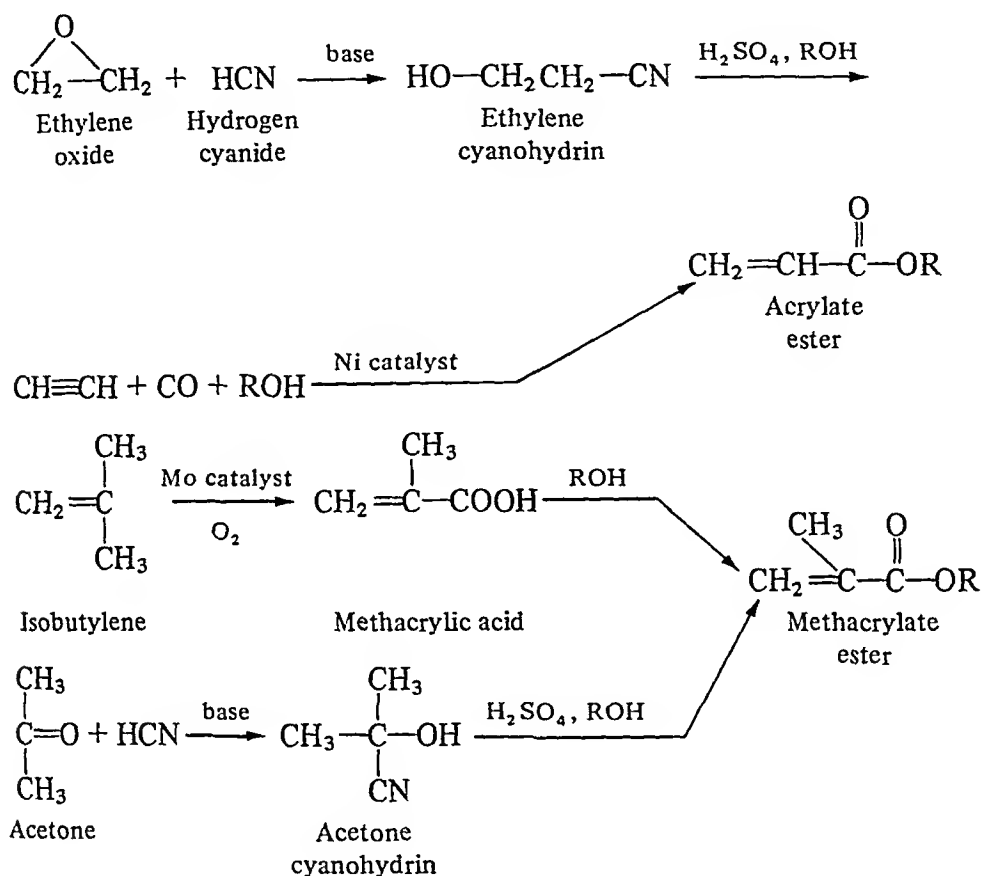
T_g = glass transition temperature

T_s = softening temperature

T_m = melting temperature

Later in the 1930s poly(methyl methacrylate) sheets and molding compounds became available. Latex paints based on ethyl acrylate for exterior application achieved importance in the 1950s and 1960s. Acrylonitrile has been mentioned previously (Sec. 13-3) as a fiber former and as a comonomer in oil-resistant rubber.

Acrylates can be made a single-step process from acetylene or a two-step process from ethylene oxide. Methacrylates can be made by selective oxidation of isobutylene followed by esterification or by a two-step process starting with acetone.



The quiescent bulk polymerization of methyl methacrylate was used as an example in Sec. 5-2. A stirred bulk polymerization like that used for styrene (Sec. 13-3) could be adapted for methyl methacrylate. A modification which bears a little more resemblance to the vinyl chloride bulk polymerization (Sec. 13-5) is *granulation polymerization* [35]. A small amount of water, some lubricant, and either a water- or oil-soluble catalyst is agitated with monomer (or a monomer-polymer syrup) in a heavy-duty dough mixer. Fluffy, granular particles result and can be washed, dried, and extruded into molding pellets. The absence of emulsifier or suspending agent gives a clear product, and the granular nature of the agitated mass gives better temperature control than a viscous, homogeneous mass would afford.

A suspension process for poly(methyl methacrylate) has been described in enough detail to point up some interesting features (Fig. 13-18). The chemicals in the aqueous phase include sodium polyacrylate (suspending agent) and buffers. Polymerization takes only about an hour at 95 to 110°C, 40 psig (0.3 MPa), which means that a 10-m³ reactor can produce more polymer than a 40-m³ reactor for styrene or

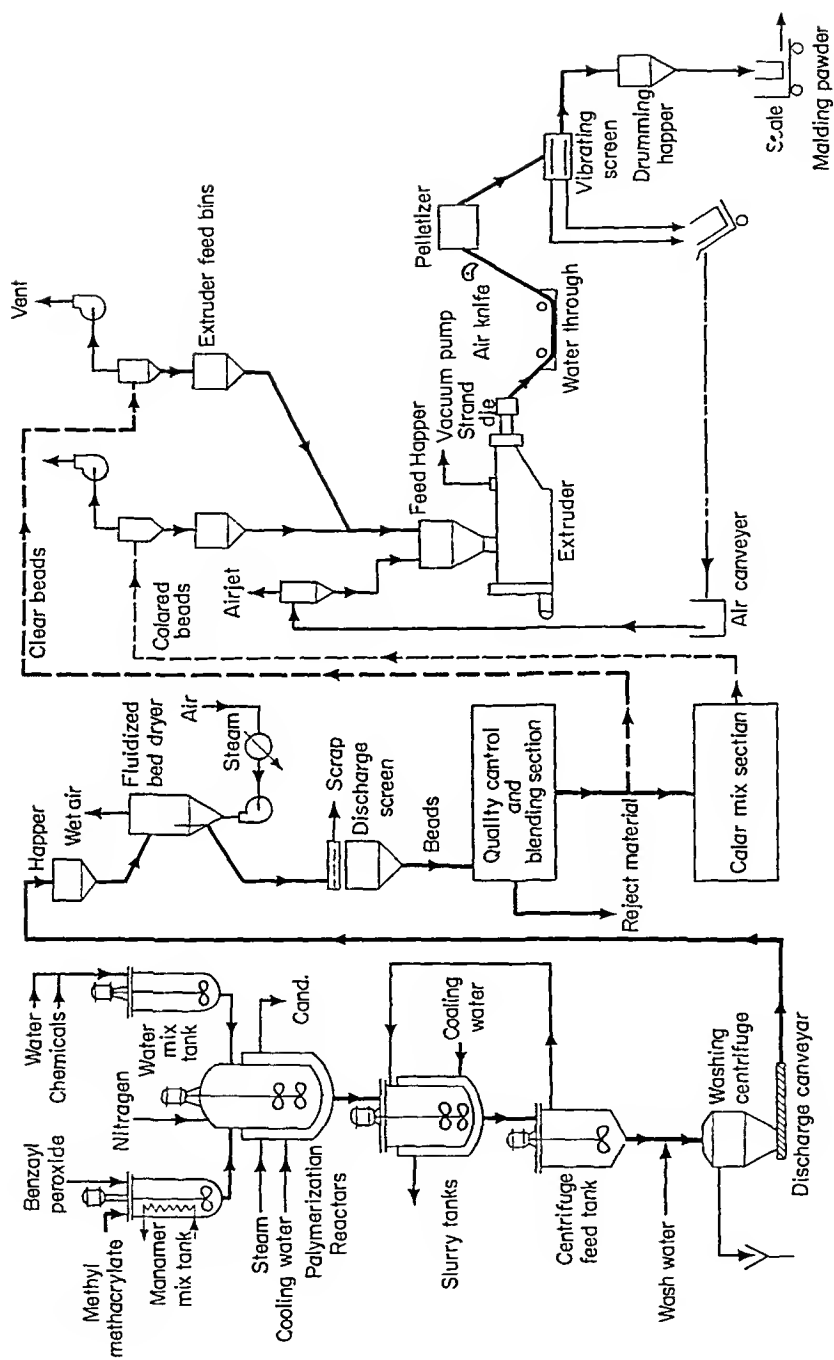


FIGURE 13-18
Suspension polymerization of methyl methacrylate [36].

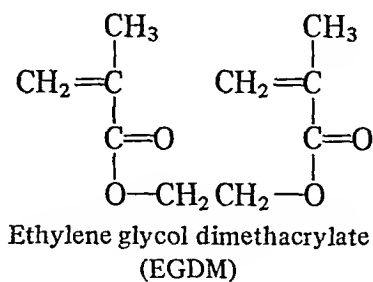
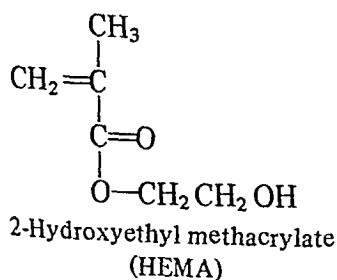
vinyl chloride with their typical reaction times of 8 to 15 h. The advantage is cut somewhat by charging and emptying times. A saving is realized by using the back pressure to push the warm suspension into a separate slurry cooling tank and immediately recharging the reactor. This plant uses a cyclic fluidized-bed dryer rather than a continuous rotary or tunnel dryer as some other processes have done. Both molding powder (pellets) and extruded sheet are made.

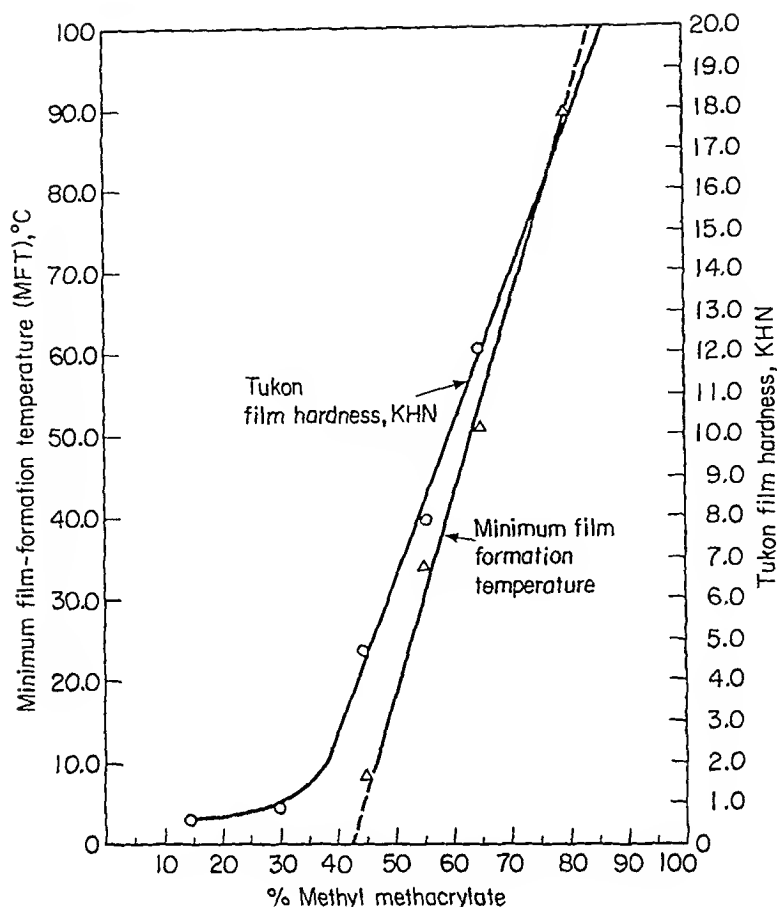
The polymerization of ethyl acrylate most often is carried out in emulsion. A process such as that used for vinyl acetate is suitable (Sec. 13-4). Like vinyl acetate, the monomer is slightly water-soluble, so that "true" emulsion polymerization kinetics are not followed. That is, there is initiation of monomer dissolved in water in addition to that dissolved in growing polymer particles. Ethyl acrylate is distinguished by its rapid rate of propagation. Initiation of a 20% monomer emulsion at room temperature by the redox couple persulfate-metabisulfite can result in over 95% conversion in less than a minute. To control the temperature a continuous addition of monomer at a rate commensurate with the heat transfer capacity of the reactor is necessary.

A copolymer of ethyl acrylate with 5% chloroethyl vinyl ether has been marketed as an oil-resistant, high-temperature stable, specialty elastomer for some years. The pendant chlorine group gives a preferred cross-linking site with polyfunctional amines. The relatively high T_g of the rubber (*ca.* -28°C) can be lowered by plasticization, but this can be temporary if oils or solvents are in contact with the product and leach out the plasticizer. Interpolymers of ethyl acrylate with methyl methacrylate and with higher acrylates and methacrylates are widely used as latex paints and as additives for paper and textiles. An important parameter of such a system is the minimum film-forming temperature, which one might expect to be related to the T_g . It can be seen (Fig. 13-19) that an almost linear relationship exists between this temperature and composition for the simple binary system. The film hardness measured at room temperature also is expected to increase as the interval between room temperature and T_g increases.

The water-soluble polymers of acrylamide, acrylic acid, and methacrylic acid probably are produced by solution polymerization. Interpolymers abound for such uses as sewage coagulation, drag reduction, adhesives, coatings, and textile and paper sizes.

In the last 30 years contact lenses have become an important method of correcting eye defects. While there are other reasons for choosing "contacts" over conventional glasses, the major reason is appearance. There are two basic types, both based on acrylic polymers. The hard lenses generally are made from poly(methyl methacrylate). Most soft lenses are made from poly(2-hydroxyethyl methacrylate), also called poly(HEMA).



**FIGURE 13-19**

Hardness and minimum film formation temperature for copolymers of ethyl acrylate and methyl methacrylate [37]. The Knoop Hardness Number (KHN) is obtained in a Tukon Indentation Tester (ASTM D1474) and is inversely proportional to the length of an indentation made by a diamond-shaped tool.

While the soft lenses require more care and may be of somewhat lower optical quality, they are usually more comfortable and easier to get accustomed to. As it is used, poly(HEMA) is slightly cross-linked because of the dimethacrylate (EGDM) present. It is a swollen hydrogel in contact with tears, but does not dissolve. Copolymers of HEMA with vinyl pyrrolidone have been used for lenses also.

The polymerization process for HEMA lenses is a casting operation. A spinning mold is used so that the outside diameter of the lens is determined by the mold surface and the inside diameter depends on the rotational speed of spinning which alters the free surface. Free-radical polymerization of the HEMA-water mixture takes place in the mold. This particular hydrogel is only one of many that have been studied. While poly(HEMA) dominates the soft contact lens market, many other hydrogels have been tested as soft tissue replacements in the human body [38].

Use Pattern

To the layman, the term acrylic plastic has become synonymous with poly(methyl methacrylate), although the trade names such as Plexiglas, Lucite, Perspex, and Acrylite

might be even better known (Table 13-18). The high light transmittance of poly(methyl methacrylate) has led to its use in a variety of decorative forms. Industrially, one single large market for molded, dyed polymer has been automotive exterior signal lenses. The toughness and stability of the polymer are important. In the automobile interior and in appliance panels, "internally lighted" numerals and letters can be molded in, since the transparent plastic transmits light so well that it is scattered only at interruptions such as raised or roughened surfaces. Exterior glazing in large structures such as the United States Pavilion at Expo '67 (Montreal) and the Astrodome (Houston) were made from white or gray translucent panels. Aircraft glazing has been formed from stretched sheets for many years. Acrylics can be toughened by rubber addition in the manner of polystyrene, but with a sacrifice in light transmission.

Some other uses of acrylate and methacrylate interpolymers are as viscosity index improvers in lubricating oil, ion-exchange resins, textile additives, paper coating, thermosetting (baking) coatings, and polymeric plasticizers in poly(vinyl chloride). A recent development is an all-acrylic film used for surfacing metals, plywood, or other substrates. Supplied in thicknesses of 50 to 150 μm , the films may be printed before lamination. These films compete with conventionally applied acrylic lacquers as well as with the decorative paper laminates based on melamine-formaldehyde resins (Sec. 12-5, Laminates). Cyanoacrylate adhesives were described in Sec. 12-4, Adhesives.

13-7 THE FLUOROCARBON POLYMERS

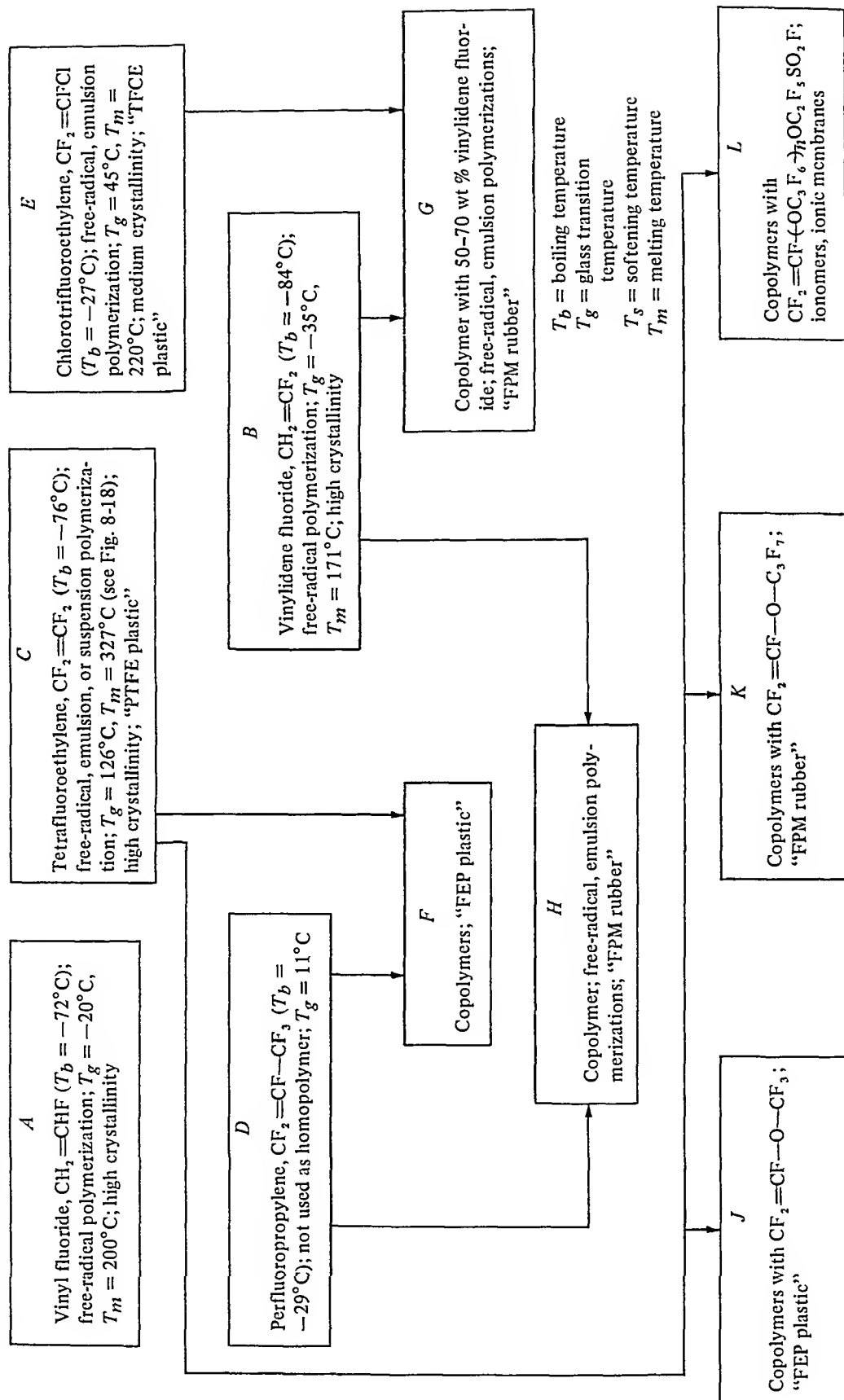
Although many fluorocarbon polymers are commercially available, poly(tetrafluoroethylene) (Table 13-19) is estimated to command about 90% of the market. This polymer, under DuPont's trade name, Teflon, has been made since the early 1940s. The combination of high temperature stability, chemical resistance, and surface lubricity has made it useful in many industrial applications and, more recently, in coated kitchenware such as frying pans, cookie sheets, pots, and pans. In order to

TABLE 13-18
End-Use Pattern for the Acrylics

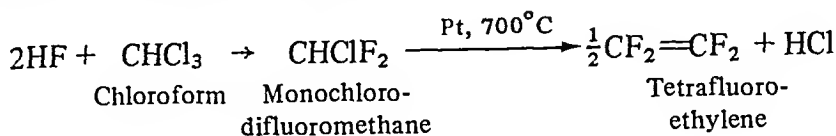
Polymer*	Molded plastic	Extruded plastic	Film	Laminates	Tires	Rubber specialties	Fibers	Adhesives and coatings	Polymer additives
A								• •	
B								• •	
C	• •	•							
D								• •	
E, H	• •	• •						•	
F						• •			
G, L								• •	
J								• •	
K (packing)								• •	•
M	•								

* See Table 13-17 for code.

TABLE 13-19
The Fluorocarbon Polymers



make the monomer, chloroform is treated with hydrofluoric acid to give an intermediate which is subjected to pyrolysis.



Emulsion polymerization of the monomer gives a latex that is used directly in some applications, notably in thin coatings. One solid form sold is the coagulated latex with aggregates about 0.5 mm in diameter made up from the latex particles, which are 0.1 μm in diameter. Another solid form also has granules about 0.5 mm in diameter apparently made by a suspension polymerization, since no finer ultimate particle is discernible [39].

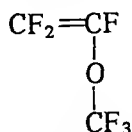
Special techniques have been developed to process the polymer into useful items. (The polymer is dense (2.2 g/cm³), insoluble at temperatures below its T_m (327°C), and highly crystalline (see Fig. 8-19 for thermal transitions). The favored method for forming resembles techniques developed for powdered metals. Particles are brought into intimate contact by high-pressure preforming or by suspension in an oil which is removed before fusing. The particles are sintered together by heating to 370°C followed by cooling. Thin coatings adhere well to metals, but the polymer is very hard to print upon or to fasten to another surface by ordinary adhesives. Good adhesion usually requires a chemical alteration of the surface. A dispersion of sodium metal in kerosene will attack poly(tetrafluoroethylene) sufficiently to allow adhesion to metals and plastics. It is one of the few reagents that have any effect on this polymer. Semifinished forms that are available include tape, film, tubing, and fibers.) The tape may be skived, that is, shaved from a molded cylinder. Extruded tape, made by sintering an extruded paste of powder in oil, is much smoother but somewhat more expensive. (Spun fibers of poly(tetrafluoroethylene) are quite expensive.) However, a less costly process has been developed which produces fibrous-porous shapes by a replicating technique.

Poly(chlorotrifluoroethylene) and the copolymer of fluorinated ethylene and propylene represent polymers that can be molded by conventional techniques while preserving a large measure of the chemical resistance and high-temperature stability of poly(tetrafluoroethylene). There is a sacrifice in these properties, however. (Films based on vinyl fluoride and vinylidene fluoride are much more stable than the corresponding chloride products. Their use has been recommended in outdoor applications where weather resistance and moisture containment are important. While the fluorine-carbon bond is very strong in these polymers, the carbon-hydrogen bond is susceptible to oxidation, making them less chemically resistant than a fully fluorinated material. On the other hand, they are much more dimensionally stable, not having the multiple transitions near room temperature that are associated with poly(tetrafluoroethylene)'s tendency to cold-flow.)

Rubbers based on fluoro or chloro-fluoro polymers make use of carbon-hydrogen bonds in a comonomer to provide cross-linking sites. Peroxides can be used to abstract hydrogen atoms, leaving chain radicals to join in carbon-carbon links. However, amines such as hexamethylenediamine are used more often. One widely

used FPM rubber (Table 13-19) can be cross-linked by heating with an alicyclic amine salt and magnesium oxide at 150°C for 30 min followed by a "postcure" of 24 h at 200°C. The vulcanizate can be used for continuous service as high as 200°C and yet can be useful down to its brittle temperature of -40°C. Solvent and chemical resistance is excellent except for amines, ketones, and a few other polar chemicals.

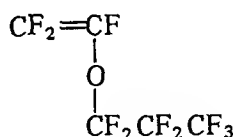
In 1970, duPont revealed a new perfluoroelastomer (now known as Kalrez) based on tetrafluoroethylene and perfluoromethylvinylether [40].



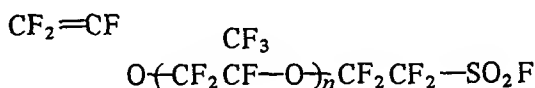
Perfluoromethylvinylether

A third undisclosed perfluorinated monomer (perhaps 1-hydropentafluoropropylene) provides a cross-linking site. The random copolymer has a molar ratio of 3:2 for the two major monomers, C_2F_4 and $\text{C}_3\text{F}_6\text{O}$, respectively, and a T_g of -12°C. The rubbery material and its cross-linked derivative are quite stable for months at 288°C.

Two other monomers that have been used with C_2F_4 are a vinyl propyl ether and an ionic ether:



Perfluoropropyl vinyl ether

Sulfonyl fluoride vinyl ether
(PSEPVE, DuPont)

The first monomer has been used to modify PTFE to make it thermoplastic but with somewhat better stability than FEP based on perfluoropropylene (Table 13-15). The second monomer makes copolymers that are ionomers, swelling in water. Films of copolymers (Nafion, DuPont) have been used as membranes in electrolytic cells and in ion recovery units [41].

TABLE 13-20
End-Use Pattern for Fluorocarbon Polymers

Polymer*	Molded plastic	Extruded plastic	Film	Laminates	Tires	Rubber specialties	Fibers	Adhesives and coatings	Polymer additives
A			• •						
B, L			• •						
C	• •	• •	•	•			•	• •	•
E	• •	•							
F, J	• •	• •						•	
G, K						• •		•	
H						• •		•	

*See Table 13-19 for code.

Use Pattern

The workhorse of the fluorocarbon family, poly(tetrafluoroethylene), is molded and extruded only by the special techniques mentioned previously (Table 13-20). [A familiar form of film is the tape used as a pipe thread "dope." The cold flow of the polymer to seal the threaded pipe joint is a real advantage here. Fibers have been made from the polymer and woven into textile for special applications such as filter fabrics, protective clothing, and surgical thread. The rubbery copolymers are most often seen as O-rings and gaskets, but tubing and sheets are also used.]

PROBLEMS

- 13-1. In Fig. 13-7, what is the purpose of sending the monomers through a caustic contactor?
- 13-2. Describe two methods for coagulating a latex (see Figs. 13-7 and 13-14).
- 13-3. Assuming 15% conversion per pass, calculate the energy needed to compress ethylene to 2000 atm and 100°C for the production of one pound of polymer. At \$0.03/kWh, is this a significant production cost?
- 13-4. Explain the origin of short- and long-chain branches in polyethylene produced at high pressures.
- 13-5. Why are so many synthetic rubbers copolymers?
- 13-6. What difference in structure might be expected between cold- (5°C) and hot-process (50°C) styrene-butadiene rubber?
- 13-7. Why are some ethylene-propylene copolymers stiff and crystalline (at room temperature), while others are soft and amorphous?
- 13-8. Vinyl acetate is polymerized, hydrolyzed, and reacted with butyraldehyde to give a soluble product.
 - (a) Why is it not hydrolyzed first, then polymerized?
 - (b) What is a major use of the product from each of the three steps?

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14

HETEROCHAIN POLYMERS

14-1 POLYESTERS

The alkyd resins (described in Sec. 12-4) were developed in the 1920s and 1930s as an outgrowth of the earlier cooked varnishes, which combined unsaturated oils with natural resins. Similar unsaturated polyesters were dissolved in styrene monomer to make casting and laminating resins in the 1940s. Films and fibers based on poly(ethylene terephthalate) were developed in England in the 1940s. During the 1950s, polycarbonates of bisphenol A were offered in Germany and in the United States.

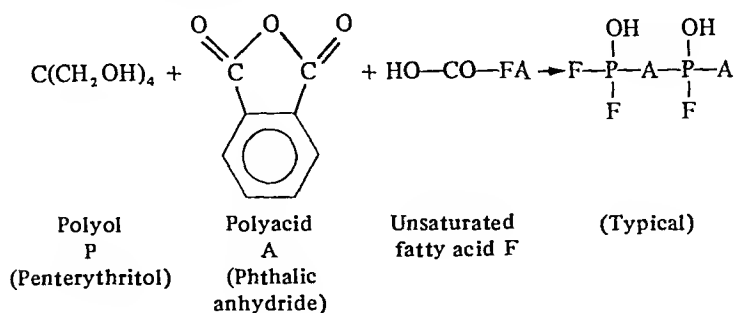
The condensation of an alcohol with an acid to give an ester with water as a byproduct is one way to make polymers (Table 14-1). In alkyd resin cooking (Sec. 12-4) it was mentioned that additional reactions are those between anhydride and alcohol or epoxide and between free acid and alcohol and esters (transesterification). The alkyd resin kettle also could be used to make a poly(ethylene maleate) for use as a casting or laminating resin. It is more likely, however, that other monomers would be included in the resin to give branching, higher reactivity, or resistance to hydrolysis. The simple polyester with its repeating dyadic structure can be dissolved in styrene (about 70 parts polyester to 30 parts styrene) and polymerized at room temperature by a free-radical route using a redox couple. (Methyl ethyl ketone peroxide plus cobalt naphthenate would be typical.) Glass-reinforced boat hulls and automobile bodies are made from such systems. In some cases, monomers more expensive than styrene can be justified. Methyl methacrylate, triallyl cyanurate, and diallyl phthalate have been suggested by various sources.

Ester interchange is favored for terephthalates because the free acid is very insoluble and difficult to incorporate into a reaction system. Two stages are used. In the first, methanol is displaced from the terephthalic acid ester by the diol. In the second, the excess diol is driven off at high temperatures and low pressures. A

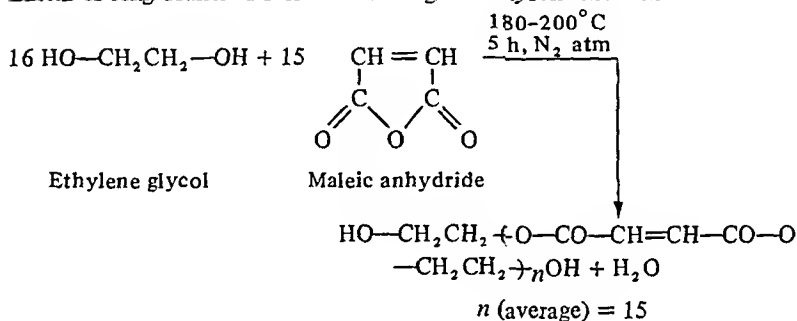
TABLE 14-1
Polyesters

I. Unsaturated polyesters

A. Branched alkyd resins for coating

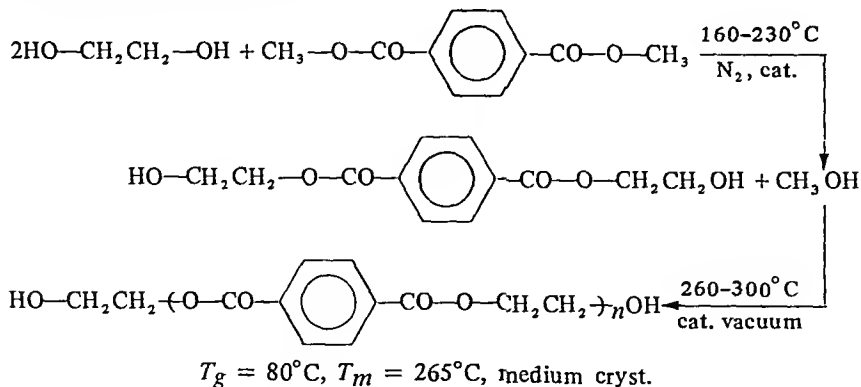


B. Linear or long-branched resins for casting with styrene monomer

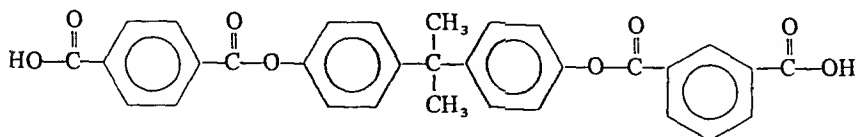


II. Saturated polyesters

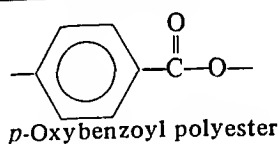
A. Terephthalates and related esters



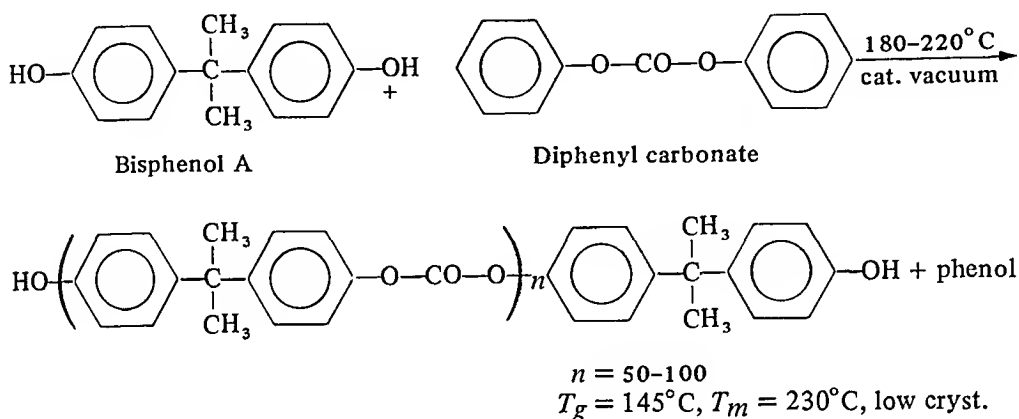
Same ester with $\text{HO}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{OH}$ in place of glycol, $T_m = 228^\circ\text{C}$.



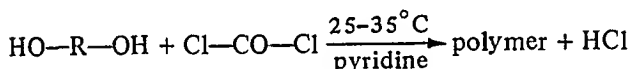
Aromatic polyester based on terephthalic and isophthalic acids with bisphenol A. T_g about 175°C . Typical units shown.

TABLE 14-1
Polyesters (Continued)

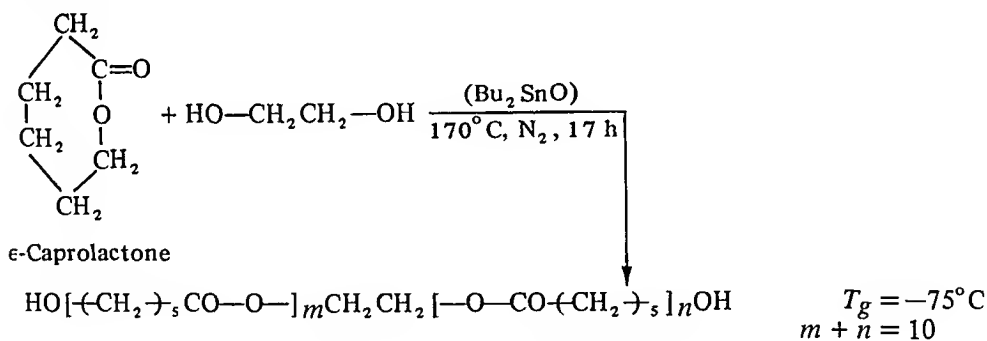
B. Polycarbonates



Also



C. Polylactone



Diol for extension by diisocyanate

continuous process (Fig. 14-1) starts with a molar ratio of DMT (dimethyl terephthalate) to glycol of 1:1.7. Methanol is removed from the horizontally sectioned vessel over a period of 4 hr with a rise in temperature to 245°C at a pressure of 1 atm. In two polycondensation reactors the pressures are about 0.020 and 0.001 atm, successively, and the exit temperatures are 270 and 285°C . The resultant polymer melt is low enough in viscosity that pumps can be used to extrude fibers directly or to make chips as an intermediate form for storage.

In the mid-1970s beverage bottles made of poly(ethylene terephthalate), PET, became common. The process of stretch-blow molding (see Sec. 12-6, Molding) made possible strong bottles of high clarity. The most popular sizes are 2

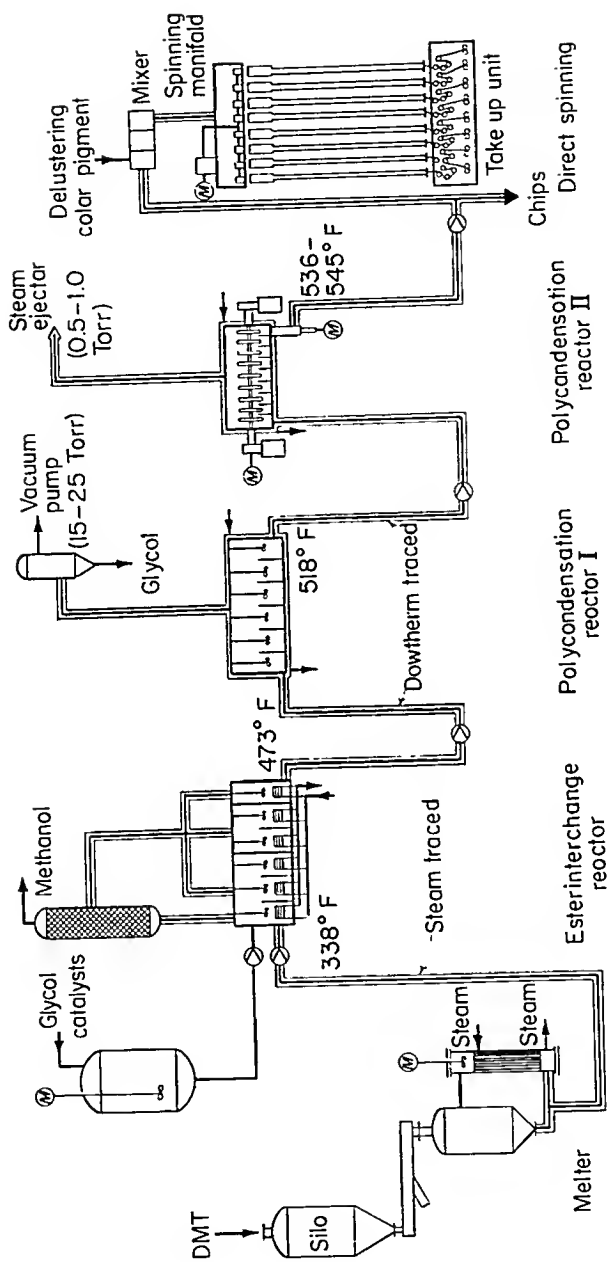
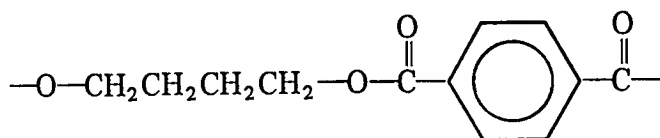


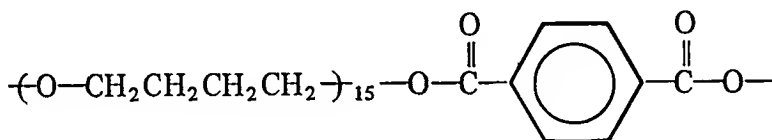
FIGURE 14-1
Continuous preparation of poly(ethylene terephthalate) [1].

liter and 32 oz. PET has the unfavorable property in thick sections of crystallizing slowly over a long period of time after molding. This results in some dimensional changes due to shrinkage and warping. In the 1970s poly(butylene terephthalate), PBT, has become popular. Although the T_m is 228°C compared to 265°C for PET, PBT is much easier to work with. Reinforced with glass fibers, the polymer competes with nylon and metal for such applications as gears, machine parts, small pump housings, and insulators.

Another related material is a thermoplastic elastomer made by using two diols differing in molecular flexibility:



Repeat unit in hard segment

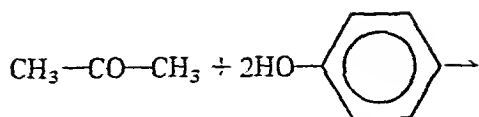


Soft segment

The final polyester [2] with a molecular weight of about 30,000 is made up of soft, flexible segments (mol wt about 1500) and an equal number of hard segments (mol wt about 700). At a molding temperature above 200°C the materials are thermoplastic. Below 150°C the "hard segments" crystallize to form massive cross-links similar to the glassy domains in the styrene-butadiene or styrene-isoprene block copolymers (see Sec. 4-5, Anionic Systems). The lower temperature limit for rubbery behavior is set by glass formation at about -50°C . Between -50°C and 150°C , the materials are rubbery and can be used for molded tires, snowmobile tracks, wire and cable insulation, gaskets, seals, and other mechanical goods.

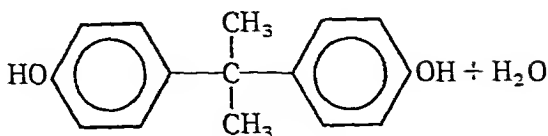
Several aromatic polyesters (polyarylates) are made which have high T_g 's because of the stiff backbones containing many aromatic rings. Poly(*p*-oxybenzoyl ester) is a compact, linear, crystalline polymer which does not melt below its decomposition temperature of 550°C . Like poly(tetrafluoroethylene) (abbreviated PTFE), the ester can be fabricated by compression sintering at temperatures above a crystal-crystal transition (330 to 360°C). The polymer can be combined with PTFE (see Sec. 13-7) in a plasma-spray coating. Typically a 1:3 ratio of polyester to PTFE is applied using an argon-hydrogen plasma. When powdered plastics are deposited and sintered on a metal surface, wear-resistant coatings with low coefficients of friction are produced.

An important ingredient for a number of heterochain polymers is bisphenol A, which is produced by the condensation of acetone with phenol. Bisphenol A can be combined directly with phosgene in the presence of an HCl acceptor such as pyridine. In analogy with the terephthalate condensation, phenol can be condensed with phosgene in a prior step to make diphenyl carbonate. This material can then



Acetone

Phenol



Bisphenol A

be purified by distillation before the reaction with bisphenol A in which phenol is eliminated.

The polymer of isophthalic acid with bisphenol A (Table 14-1) is amorphous with a heat deflection temperature (near T_g) of 173°C . Melt temperatures for molding can be as high as 350 to 400°C . Copolymers of *p*-hydroxybenzoic acid with the bisphenol A, terephthalic acid ester are also made.

A variety of aliphatic polyesters of molecular weight near 1000 are made with terminal hydroxyl groups to form the basis for urethane polymers. A ring scission polymerization has been used for one such material (Table 14-1). A product which is less likely to crystallize on aging can be made if a copolymer of α -methyl caprolactone and caprolactone is made.

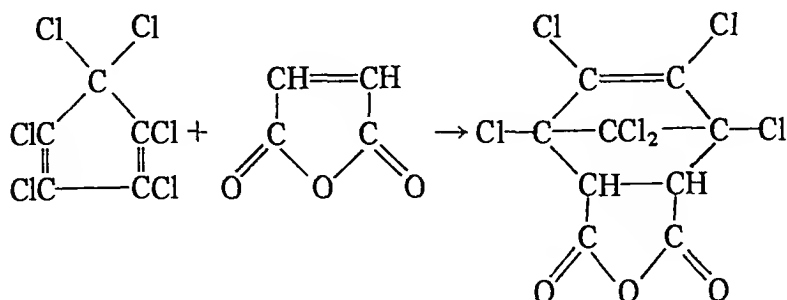
Use Pattern

Aliphatic polyesters have been used as lubricants and as vinyl plasticizers (Table 14-2). Hydrolytic stability is a factor to be considered in many applications. As a rule, aryl acids and branched-chain diols resist hydrolysis. Fibers and films of terephthalic acid esters and polycarbonates are not particularly sensitive to moisture. Alkyd resins are so highly cross-linked in the final coating that water is not a major problem, although alkaline solutions of soaps and detergents can cause film failure.

TABLE 14-2
End-Use Pattern for Polyesters

Polymer	Molded plastic	Extruded plastic	Film	Laminates	Tires	Rubber specialties	Fibers	Adhesives and coatings	Polymer additives
Alkyd resins								• •	
Linear, unsaturated polymers	•			• •					
Poly(ethylene terephthalate)			• •				• •		
Polycarbonate	• •	•							
Diol-terminated polymers	• •					•			

It is in the urethane foams that hydrolytic stability has been a significant factor. Flammability is a parameter that is important for all materials. Polyesters for casting resins can be modified by copolymerization with a chlorine-rich diacid to decrease flammability. The Diels-Alder condensation product of hexachlorocyclopentadiene with maleic anhydride has a chlorine content of 55% and is a popular monomer for this purpose.



Polycarbonate has been used for some years as "safety" glazing. In thin sheets the plastic has extremely high impact strength. Both in the form of sheets and as molded lamp housings it has been a favored material for vandal-resistant, rugged applications. In 1979 a silicone treatment for polycarbonate surfaces was announced that is claimed to make the abrasion resistance of the polymer approach that of ordinary inorganic window glass. Automobile windows are a definite goal as a large-scale, single market.

14-2 POLYETHERS

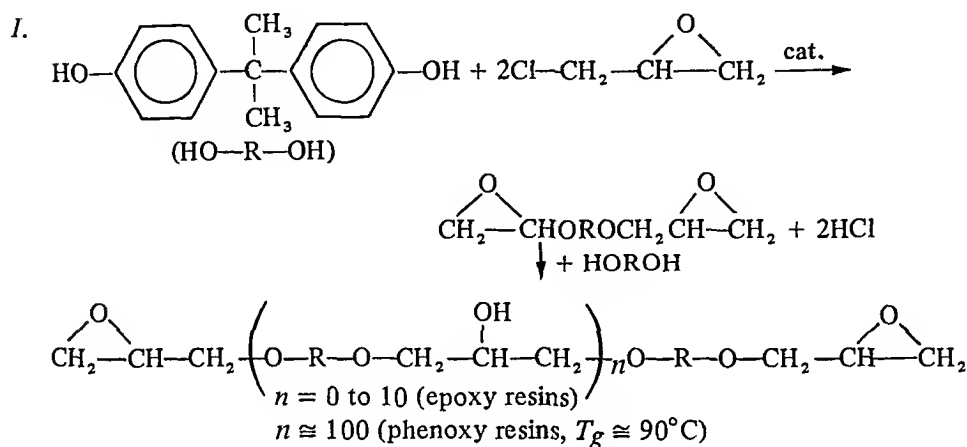
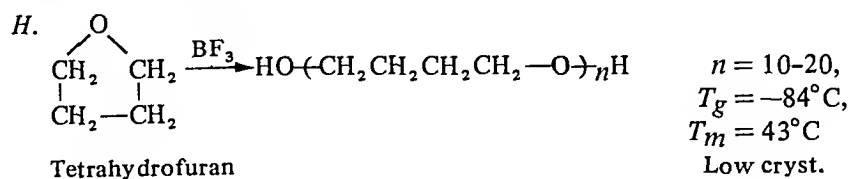
Polymers of formaldehyde form spontaneously in aqueous solutions of the monomer, but a useful molding material was not marketed until the late 1950s. The three-membered ring of ethylene and propylene oxide opens readily and was used for low-molecular-weight surfactants in the 1940s. Urethane prepolymers became important in the 1950s; high-molecular-weight poly(ethylene oxide) became available in 1958; and rubbers based on epichlorohydrin came on the market in 1966. The epoxy resins from bisphenol A and epichlorohydrin were produced in the 1940s, and the high-molecular-weight phenoxy resins appeared in the 1960s. Polysulfide rubber was the first successful synthetic rubber in the United States back in the 1920s. The aromatic polyethers poly(phenylene oxide) and polysulfone appeared in the 1960s. Although polysaccharides and silicones could be regarded as polyethers, they will be treated separately.

Formaldehyde forms low-molecular-weight polymers and ring compounds so easily that it must usually be prepared as an integral part of the polymerization process. Thermal decomposition of a waxy, anhydrous polymeric formaldehyde yields a dry, monomeric vapor that can be dissolved in an inert hydrocarbon such as heptane along with an initiator. Initiators include Lewis acids such as BF_3 (Table 14-3, 14) as well as amines, phosphines, arsines, stibenes, organometallic compounds, and transition metal carbonyls. Esterification of the end-group hydroxyls may take place in a separate, subsequent operation. The polymer is often referred

TABLE 14-3
Polyethers

I. Ring-scission polymerization

- A.
- $$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C}-\text{H} \\ \text{H} \end{array} \xrightarrow[\text{BF}_3, \text{H}_2\text{O}]{\text{heptane, } 25^\circ\text{C}} \text{HO}-(\text{CH}_2-\text{O})_n\text{CH}_2-\text{OH} \xrightarrow{\text{AcOAc}} \text{AcO}-(\text{CH}_2-\text{O})_n\text{CH}_2-\text{O}-\text{Ac}$$
- Formaldehyde Polyacetal
- $n = 500 \text{ to } 3000$
 $T_g = -50^\circ\text{C}, T_m = 180^\circ\text{C}$
 Highly crystalline
- B.
- $$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CH}_2 \end{array} \xrightarrow[\text{cat.}]{\text{trace H}_2\text{O}} \text{HO}-(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$$
- Ethylene oxide $n = 1 \text{ to } 10^5$ $T_g = -67^\circ\text{C}, T_m = 66^\circ\text{C}$
 Highly crystalline
- C.
- $$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CH}-\text{CH}_3 \end{array} \xrightarrow[\text{basic cat.}]{\text{trace H}_2\text{O}} \text{HO}-(\text{CH}_2-\underset{\text{CH}_3}{\text{CHO}})_n\text{H}$$
- Propylene oxide amorphous, atactic $T_g = -72^\circ\text{C}$
- $\xrightarrow{\text{AlEt}_3}$ same, cryst., isotactic $T_m = 75^\circ\text{C}$
- D.
- $$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CH}_2\text{CH}_2\text{Cl} \end{array} \rightarrow \text{HO}-(\text{CH}_2-\underset{\text{CH}_2}{\underset{\text{Cl}}{\text{CHO}}})_n\text{H}$$
- Epichlorohydrin $n = 5000\text{--}20,000$ $T_g = -15^\circ\text{C}$
 (Also copolymer with 30% ethylene oxide, $T_g = -50^\circ\text{C}$)
- E.
- $$\text{C}(\text{CH}_2\text{OH})_4 + \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CH}_2 \end{array} + \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CH}-\text{CH}_3 \end{array} \rightarrow \text{HO}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{OH}$$
- Typical urethane random copolymer polyol
 mol wt = 1000
- F.
- $$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CH}_2 \end{array} \xrightarrow{\text{"E"}} \text{HO}-\text{EEEEEE}-\text{OH} \xrightarrow{\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CH}-\text{CH}_3 = \text{P} \end{array}} \text{HO}-\text{PPPPPP}-\text{EEEEEE}-\text{PPPPPP}-\text{OH}$$
- Surfactant block copolymer
- G.
- $$\begin{array}{c} \text{CH}_2-\text{O} \\ \diagup \quad \diagdown \\ \text{ClCH}_2-\text{C}-\text{CH}_2 \\ | \\ \text{CH}_2 \\ | \\ \text{Cl} \end{array} \xrightarrow[\text{BF}_3, \text{hexane}]{-80 \text{ to } +25^\circ\text{C}} (\text{O}-\text{CH}_2-\underset{\text{CH}_2}{\underset{\text{Cl}}{\text{C}}}-\text{CH}_2)_n$$
- $n = 1000,$
 $T_g = 7.5^\circ\text{C},$
 $T_m = 130, 188^\circ\text{C}$
 Med. cryst.

TABLE 14-3
Polyethers (Continued)

II. Condensation polymerization

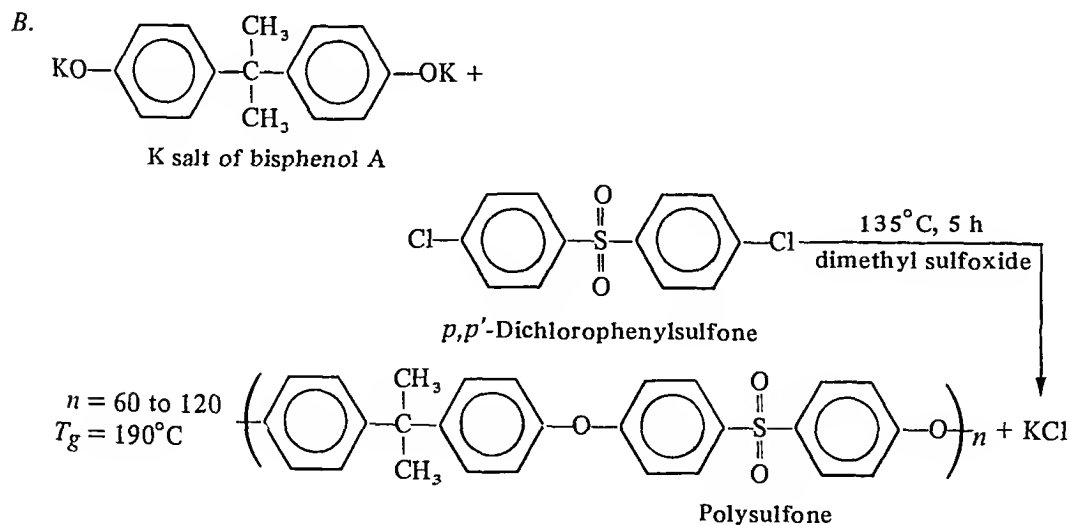
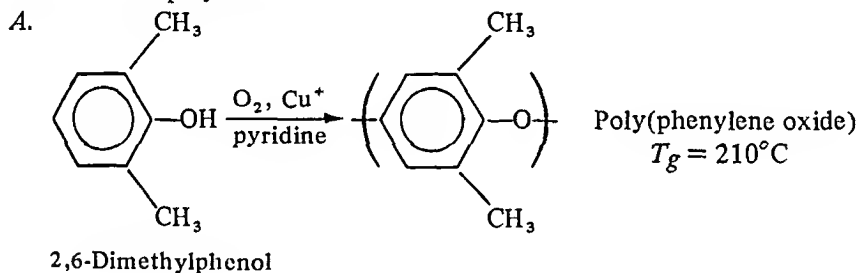
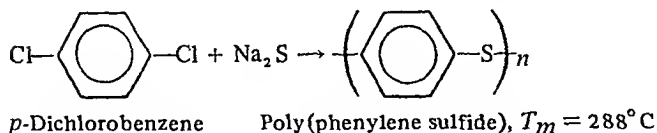
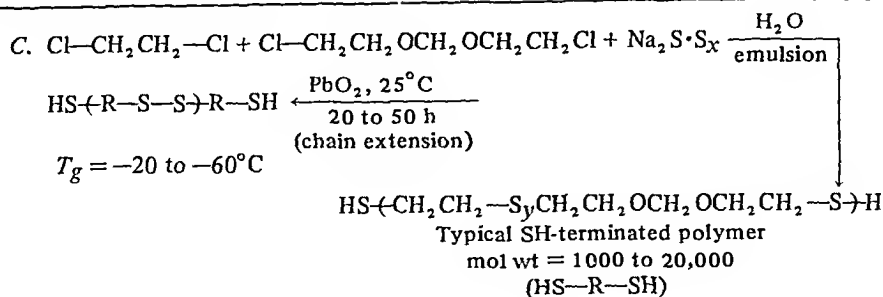
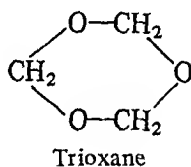


TABLE 14-3
Polyethers (Continued)

to as acetal homopolymer, polyacetal, or poly(oxymethylene). All of these terms distinguish the useful, stable polymer from polyformaldehyde, the thermally unstable, waxy material.

Some processes for making high-molecular-weight polymers from formaldehyde start with trioxane, so that an authentic ring scission is involved. The basic problem with making useful molding materials based on formaldehyde is the

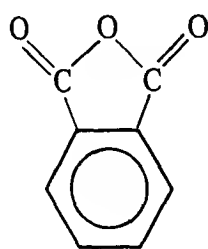


instability of the chain structure and its tendency to “unzip.” End blocking with acetic acid is one answer (Table 14-3). Another seems to be the copolymerization of formaldehyde with monomers that will interrupt the chain sequence. Ethylene oxide is one such monomer.

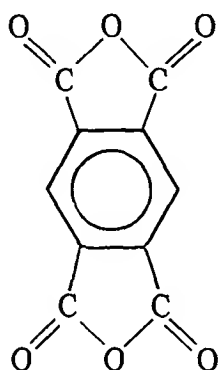
Polymers containing ethylene oxide have one prominent property, an affinity for water. Homopolymers, even with molecular weights in excess of a million, are soluble in water. Segmented, block copolymers with propylene oxide provide a wide range of materials with variable hydrophilic-lipophilic balance (HLB) because the propylene oxide polymers are not water-soluble above a molecular weight of about 500. Random copolymers of ethylene oxide and propylene oxide, homopolymers of propylene oxide, and homopolymers of tetrahydrofuran in the molecular weight range of 1000 to 3000 are often extended by reaction with diisocyanates in making foams, rubbers, and spandex-type fibers (Table 14-3).

Epoxy resins make use of several different reactions. To make the simplest member of the series, 2 mol of epichlorohydrin are reacted with 1 mol of bisphenol A at 60°C with flake NaOH added to neutralize the HCl that is formed. Actually, more than 2 mol of epichlorohydrin is charged, and the excess is removed after the

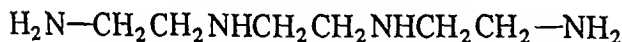
reaction. Higher-molecular-weight resins call for sturdy equipment to agitate the molten polymer. In the "taffy" process (Fig. 14-2), epichlorohydrin and bisphenol A are charged to the reactor with flake NaOH and a small amount of inert solvent. The temperature is allowed to rise to 90 or 95°C. The taffy, which forms rapidly, is an emulsion of about 30% concentrated brine in molten polymer (perhaps containing some solvent). Several cycles of washing with water are followed by stripping of solvent and water under a vacuum at 150°C. Very high molecular weights can be made by reacting low-molecular-weight polymers with additional bisphenol A with the aid of a catalyst. It can be seen that both condensation and ring scission are used for these materials. The largest use of epoxy resins (adhesives, coatings, laminates) calls for a "curing" through the oxirane rings. Popular "curing agents" include acid anhydrides and polyamines, which form ester and imine bonds, respectively. Polyfunctionality leads to network structures of high thermal stability.



Phthalic anhydride

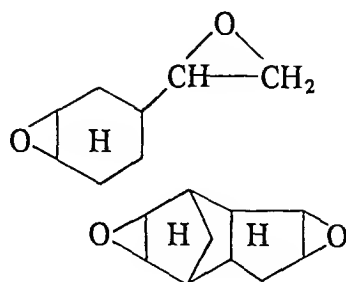
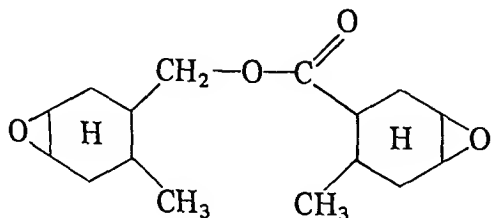


Pyromellitic dianhydride



Hexamethylenetetramine

A number of other epoxy compounds have been made by treating an unsaturated structure with peracetic acid. Some are complex, such as epoxidized soybean oil, which is widely used as a plasticizer-stabilizer for poly(vinyl chloride). Some other structures are



Specialty rubbers are made from epichlorohydrin (Table 14-3, ID).

To be useful at high temperatures, thermoplastic polymers must combine chain stiffness (for a high T_g) with thermal stability to enable molding at temperatures higher than the projected use temperature. Phenylene groups in the

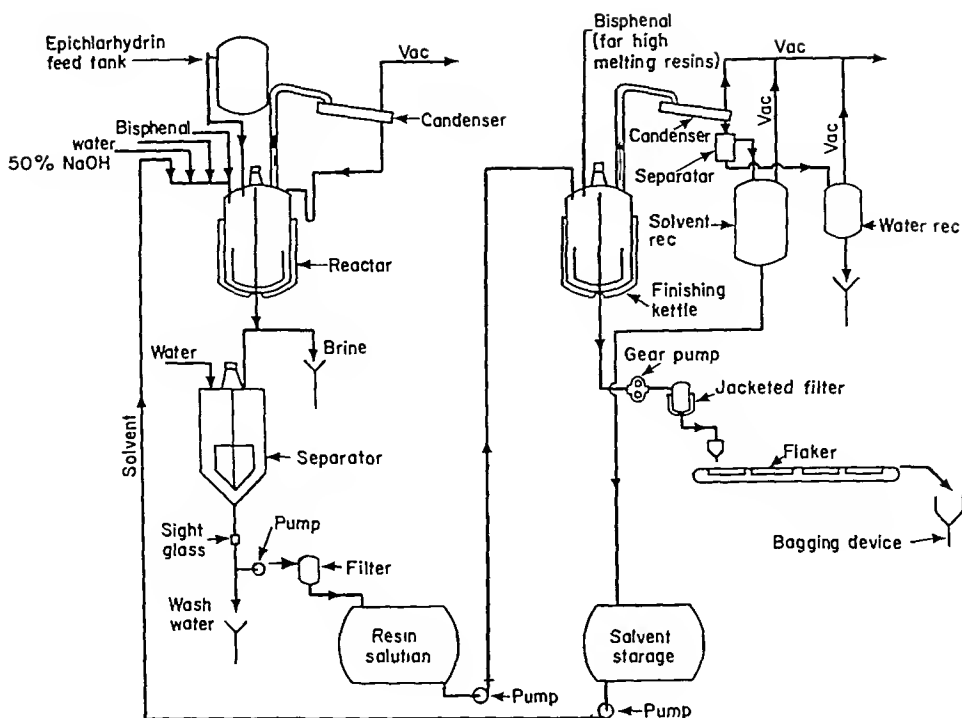


FIGURE 14-2

Equipment and process for solid epoxy resins [3].

polymer backbone contribute both of these properties. In poly(phenylene oxide), a novel oxidative-coupling technique is applicable which gives a chemically stable thermoplastic resin (Table 14-3, IIA). The polymer is difficult to process. A number of alloys (polymer blends) with polystyrene are marketed (Noryl, General Electric Co.) which combine dimensional stability and processability. The polysulfones also combine phenylene groups in a backbone to yield a thermoplastic molding material useful up to temperatures of 140 to 170°C (Table 14-3, IIB). Alloys of polysulfones with ABS resin form a separate family of materials.

The aliphatic thioethers (polysulfides) are unique among condensation polymers in being produced in an emulsion polymerization. The rank x of the inorganic sulfide used in the condensation (for example, $\text{Na}_2\text{S} \cdot \text{S}_x$) has an influence on the number of sulfur atoms in each polymer linkage. The slow oxidation of the end groups by lead peroxide at room temperature to give a high-molecular-weight (somewhat cross-linked) polymer is a very desirable change when the tacky or liquid polymers are cast or applied as pastes in the case of sealants. The sulfur analog of poly(phenylene oxide) is poly(phenylene sulfide), which can be made by a condensation reaction between *p*-dichlorobenzene and sodium sulfide. The highly crystalline polymer is solvent resistant and has a low coefficient of friction. It can be injection-molded at about 300°C and also can be used as a powder spray coating.

Use Pattern

The importance of regularity, polarity, and chain stiffness becomes apparent in the uses of polyethers (Table 14-4). Only polyformaldehyde, poly(ethylene oxide), and

the polymer based on 2,2-dichloromethylpropylene-1,3-oxide are crystalline. Since poly(ethylene oxide) is water-soluble, only the remaining two polyethers are useful structural materials. Phenoxy, phenylene oxide, and sulfone polymers are useful thermoplastics because the chain stiffness contributed by aromatic rings in the backbone raise T_g well above room temperature. The aliphatic ether backbone is more conducive to low T_g 's, which are suitable for rubbery applications. Fully cured epoxy resins are dimensionally stable network polymers.

Chlorinated polyether (Table 14-3, IG) is best known by the trademark Penton. Because of its resistance to inorganic and organic reagents, it is used in injection-molded valves and pump heads and as a lining for pipe, valves, and pumps. Coatings 500 to 750 μm thick can be applied using the fluidized-bed technique (Sec. 12-4). Monofilaments made from chlorinated polyether have been used for filter supports and column packings.

14-3 POLYSACCHARIDES

Of the polysaccharides, cellulose receives the most attention from polymer chemists, since it is the basic polymer contained in cotton and wood. Cotton may have a cellulose content as high as 90% when dry, whereas wood contains about 50% of other compounds, notably lignin (about 30%), a natural phenolic polymer that is the binder in wood, as well as sugars and salts. What appear to be minor structural changes in cellulose-related polymers lead to major differences in properties. The water-solubility of some starch components and the well-known gelling action of

TABLE 14-4
End-Use Pattern for Polyethers

Polymer	Molded plastic	Extruded plastic	Film	Laminates	Tires	Rubber specialties	Fibers	Adhesives and coatings	Polymer additives
Polyacetal	• •	•							
Poly(ethylene oxide)			•					•	•
Diol-terminated polymers and copolymers (in urethanes)	•					•		•	•
Block copolymers									•
Poly(2,2-dichloromethyl propylene-1,3-oxide)	• •	• •							
Epoxy resins	•			• •				• •	•
Phenoxy resins	• •	•						• •	
Poly(phenylene oxide)	• •	• •					•	•	
Polysulfone	• •	• •						•	
Polysulfide						• •		• •	
Poly(phenylene sulfide)	• •	•						•	

pectin and agar in water are due primarily to differences in the stereoconfiguration. In addition to the hydroxyl groups of cellulose, polysaccharides may contain carboxyl groups (pectin), sulfate groups (carrageenan from Irish Moss and agar), or amide groups (chitin) [4, 5]. Typical structures are shown in Fig. 14-3. The half-ester sulfate group in agar is not shown, since it occurs only once every tenth repeat unit on the average. All of the polysaccharides result from biosynthesis in plants and animals. Some attempt has been made to carry out the production of polysaccharides by industrial fermentation. One such polymer contains mannose and mannose-6-phosphate and is used as a water-soluble emulsifier, thickening agent, or gelling agent for foods and other products (Sec. 4-8). The flow sheet (Fig. 14-4) makes provision for refining the crude product. Corn sugar, yeast extracts, and salts are charged to a fermenter as a dilute solution (2.25% dextrose, 0.4% yeast extracts, 0.5% dibasic phosphate, and 0.05% MgSO_4). The batch is inoculated with a yeast, *Xanthomonas campestris*, and the reactor is stirred and aerated with 0.5 vol of air per volume of solution per minute. After 4 days the viscosity has increased to 70 poises and the solution can be spray-dried to recover a crude polymer which is about 60% polysaccharide. Dilution and precipitation by a quaternary ammonium compound can be used to produce about 68 lb of refined polymer per 100 lb of sugar. The disadvantages of the process are the dilute solutions and long holdup times. On the other hand, a stereoregular structure of this complexity would be very expensive to produce by any present-day synthetic method.

Historically the plastics industry often dates its birth to about 1865 (Parkes, England) or 1868 (Hyatt, U.S.) when the plasticization of cellulose nitrate by camphor permitted the molding of simple objects. Regenerated cellulose in the 1900s and cellulose acetate in the 1920s pretty much displaced the nitrate from all markets except lacquers and explosives.

At first glance there would seem to be little incentive for regenerating cellulose. However, wood pulp or the short fibers left from cotton recovery (linters) cannot be molded or spun into useful forms unless they are changed chemically. In the viscose process (Table 14-5), cellulose in sheet form resembling blotter paper is steeped in aqueous alkali for 2 to 4 h in a rack in which it can then be pressed to squeeze out excess liquid. After the alkali cellulose is shredded, it is aged 2 or 3 days, during which the crystalline structure is disrupted and the molecular weight may be decreased. With carbon disulfide added in a rotating drum called a barratte, the xanthate is formed which dissolves in alkali. The orange, unpleasant smelling solution (7 to 8% cellulose, 6.5 to 7% NaOH) is ripened for 4 to 5 days, during which time the distribution of xanthate groups presumably becomes more uniform. For rayon fibers the solution is spun through spinnerets with many small holes into a salt-acid bath. A number of operations may be carried out on the fibers, including washing, bleaching, drawing, and twisting and crimping. For cellophane a slot orifice is substituted for the spinneret, and aftertreatment may include plasticization by glycerol or coating by a moisture barrier such as cellulose nitrate. In the United States alone, rayon fiber production is around 250×10^6 kg/year and cellophane production is around 100×10^6 kg/year. Sausage casing for millions of "skinless" hot dogs is made by the same process.

In the production of vulcanized fiber, the cellulose is not dissolved but is

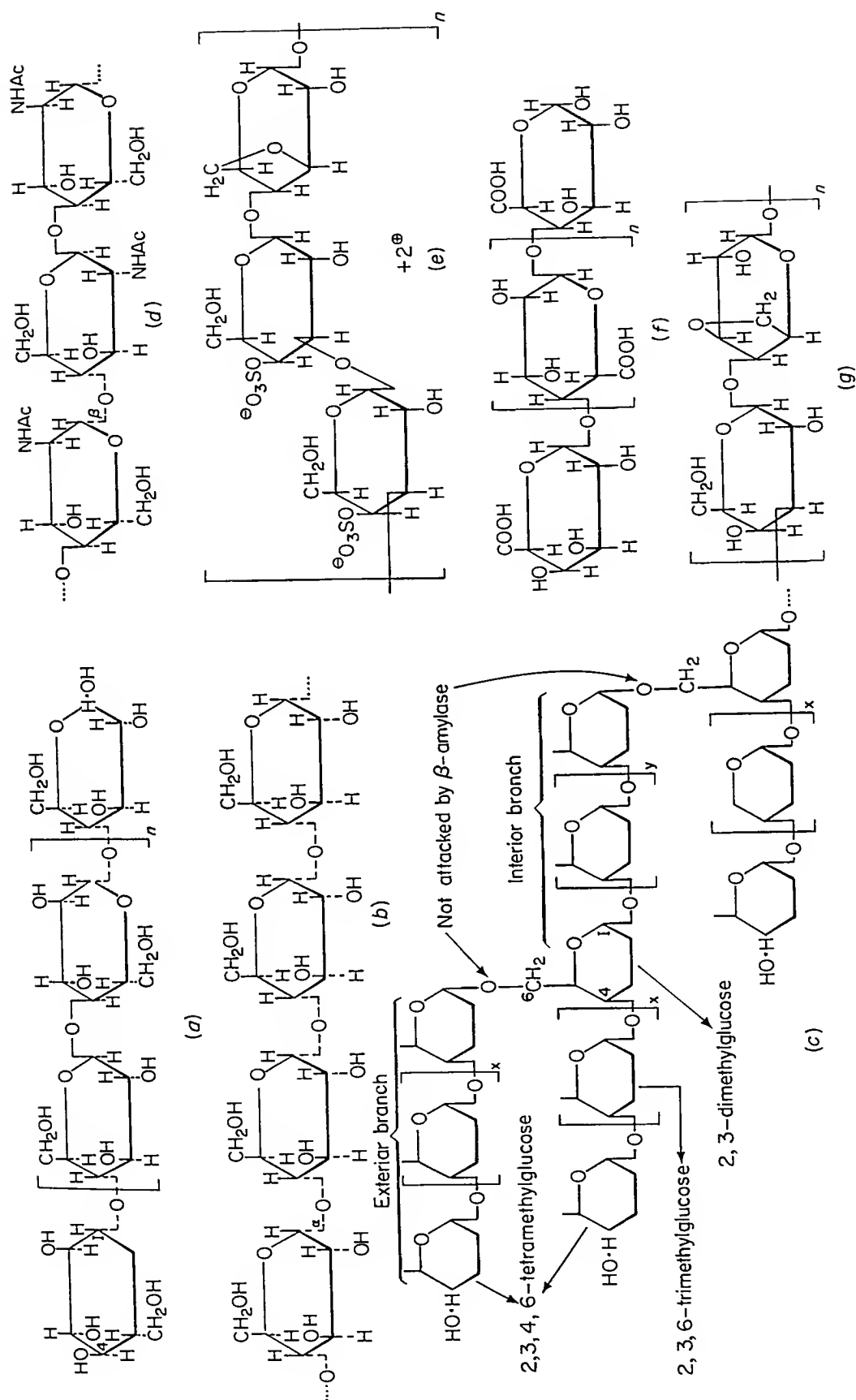


FIGURE 14-3

Polysaccharide structures [4, 5]. (a) Cellulose; (b) starch; (c) amylopectin and glycogen; (d) chitin; (e) carrageenan; (f) pectic acid; and (g) agar. (Structures (a) through (d) taken from [5] by L. F. Fieser and M. Fieser, copyright 1963 by Reinhold Publishing Corp., by permission of Van Nostrand Reinhold Company. Structures (e), (f), and (g) taken from [4] by permission of Academic Press, New York.)

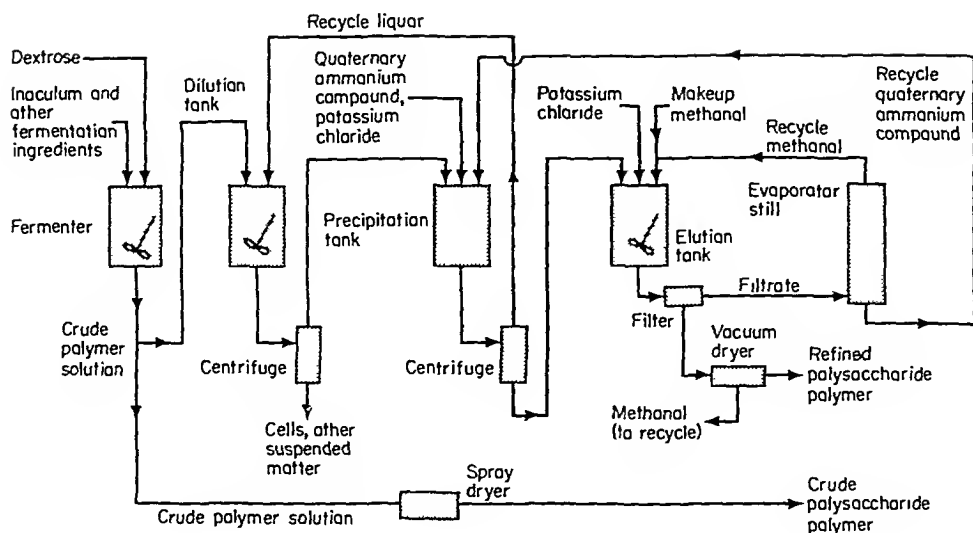
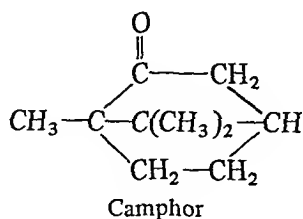


FIGURE 14-4

Microbial fermentation for production of polysaccharide [6].

highly plasticized with a concentrated zinc chloride solution so that it can be formed into sheets as thick as two inches. Washing out the salt solution is a slow process. The product retains some of the fibrous appearance of the starting material but is very dense and strong. It is oil-resistant but does absorb water. Sheets can be punched or machined for use as gaskets, bobbins, shuttles, and printed-circuit boards.

The flammability of cellulose nitrate and the necessity of having a solvent present during forming operations have pretty much eliminated it as a molding plastic. Popular household cements for paper and wood may be solutions of the nitrate in ketones and esters. Lacquers for wood and metal also do not suffer from the limitations mentioned. One molded product that is slow to yield to the use of other polymers is the ping-pong ball with its peculiar requirements of resilience and toughness. The preferred plasticizer is still camphor.



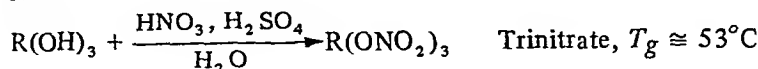
Acetylation of cellulose requires three steps. A preliminary treatment of cellulose with glacial acetic acid for 1 or 2 h is followed by reaction with acetic anhydride with a trace of sulfuric acid as a catalyst. In order to keep the temperature of the reaction at about 50°C, methylene chloride is refluxed. A typical charge would be [7]:

Cellulose	100 parts	} pretreatment
Glacial acetic acid	35 parts	
Acetic anhydride	300 parts	} acetylation
Methylene chloride	400 parts	
Sulfuric acid	1 part	

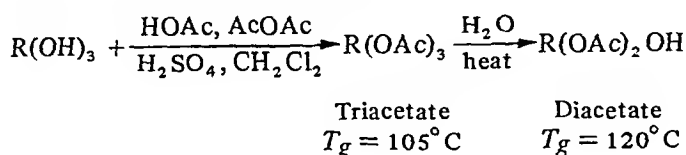
TABLE 14-5
Cellulose* Derivatives

I. Esters

A. Nitrate

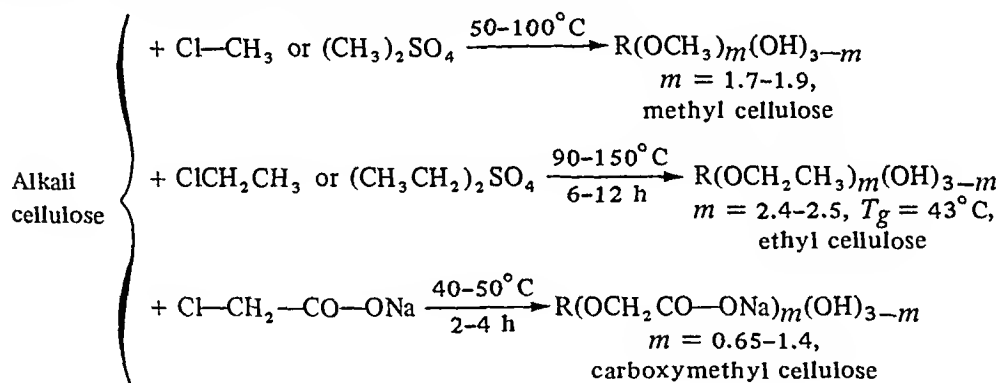


B. Acetate (also propionate, butyrate)

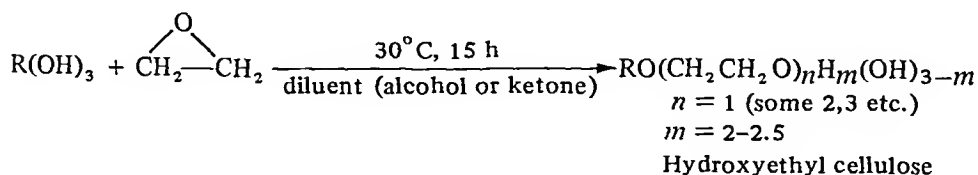


II. Ethers

A. Reactions with alkali cellulose ($R(OH)_3 + NaOH, H_2O$)

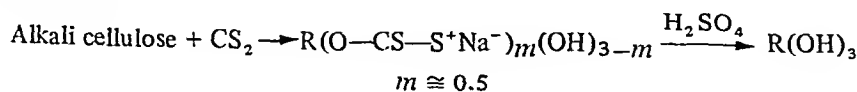


B. Reaction with slurried cellulose

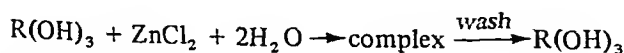


III. Regenerated cellulose

A. Viscose



B. Vulcanized fiber



*Cellulose = $R(OH)_3$.

Ethyl cellulose resembles cellulose acetate in many of its qualities (toughness, transparency) and applications (films, coatings). The other cellulose ethers are water-soluble and have the usual string of applications such as thickening agents, textile and paper sizes, cosmetic and pharmaceutical suspending agents, and water-based paint additives. Except for the hydroxyethyl cellulose, the ethers are made by condensation of alkali cellulose with a chlorinated or sulfated compound. An acid, HCl or H₂SO₄, is eliminated in the reaction. Where low degrees of substitution are encountered, the ether groups may not be evenly distributed but may be clustered toward the outside of the original cellulose fiber structure. In this respect they differ from viscose rayon and cellulose acetate, where ripening or aging steps are included to increase uniformity.

As befits a senior citizen of the polymer industry, the polysaccharide group is stable but rather sedate (Table 14-6). The imminent demise of cotton, rayon, and cellophane at the hands of new synthetics has been predicted often but has not materialized. When cotton was attacked by nylon and polyesters for use in apparel, wash-and-wear finishes based on melamine and urea resins gave it new life. Polyethylene film was supposed to take over cellophane markets but instead found new markets and left some old ones to cellophane. The outer cover on cigarette packages is one such case. Almost all cellophane is coated to lower the moisture

[illegible]

sensitivity and permeability and to provide a plastic surface that can be heat sealed. Saran (vinylidene chloride-vinyl chloride copolymer), cellulose nitrate, poly(vinyl acetate), and other ethenic polymers are used as coatings. A significant application for cellulose acetate film has been found in seawater desalination by reverse osmosis. The film is strong enough to resist the high pressures involved, and it has a good permeability to water and a low permeability to salt.

14-4 POLYAMIDES AND RELATED POLYMERS

Naturally occurring proteins and synthetic nylons are polyamides, as familiar to most of us as are our own bodies and clothing (Table 14-7). Proteins are found in all living cells. Simple proteins yield only α -amino acids upon hydrolysis. Proteins can be divided into two major classes: the fibrous and the globular proteins. The fibrous proteins act as structural materials in animals in much the same way that cellulose acts for plants. Keratin, the protein of hair, horn, feathers, and fingernails; fibroin, the protein of silk; and collagen, the protein of connective tissue, are all fibrous proteins with the common property of water insolubility. Collagen yields gelatin when boiled in water. *Globular* proteins are soluble in water or aqueous solutions of acids or bases. Albumin (eggs), casein (milk), and zein (corn) are examples of globular proteins. The common amino acids and representative analyses of some proteins are shown in Tables 14-8 and 14-9. Although great progress has been made in analyzing proteins, their synthesis has proceeded much more slowly. The first total synthesis of an enzyme, ribonuclease A, was reported in 1969 [9]. In this work, accomplished almost simultaneously by research groups at Rockefeller University and at Merck and Company, 19 amino acids were assembled into the protein which has 124 units in a definite sequence (Fig. 14-5). In one technique, each amino acid was added in sequence after the first, valine, was fully bound to an insoluble substrate. To do this, 369 chemical reactions requiring 11,931 steps were carried out in an automated apparatus. Much can be learned about protein behavior and conformation by studying simpler molecules, such as polypeptides, which are polymers of a single α -amino acid. Predictions of helix formation and of solution properties are possible in many cases [10].

The poly(α -amino acid)s are sometimes referred to as nylon 2. The term *nylon* originally was a trademark for the polyamide based on hexamethylene diamine and adipic acid. Later on it became a generic term. The numerals following the name designate the number of carbon atoms in the chain between successive amide groups. The dyadic nylons have two numbers, the first for the diamine and the second for the diacid. Monadic nylons such as polycaprolactam require only one number. Although they have been studied as protein models, the synthetic nylon-2 polymers have not been commercialized as fibers or plastics. While some new polymers have been introduced recently (nylon 4, nylon 11, nylon 12), nylon 66 and nylon 6 have been produced for a longer time and dominate the markets for synthetic polyamides.

In the 1930s a team of chemists at DuPont led by W. H. Carothers investigated the properties of aliphatic polyesters at some length before discovering that an aliphatic polyamide of the same molecular weight as the polyester would

TABLE 14-7
Polyamides and Polyimides

I. Dyadic polyamides

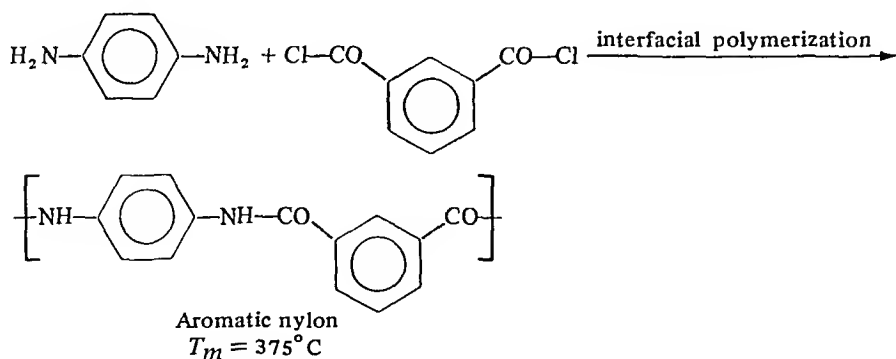
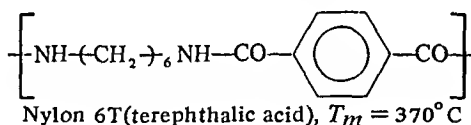
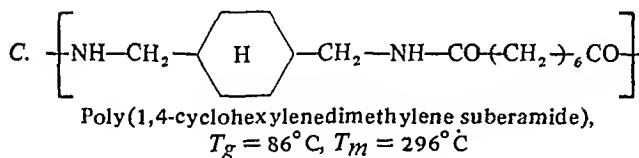
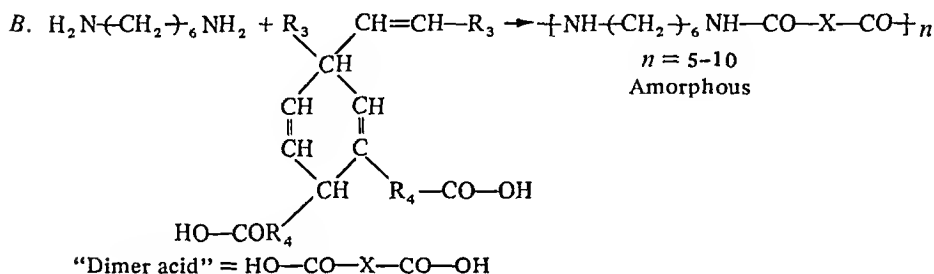
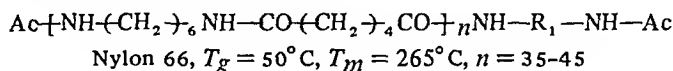
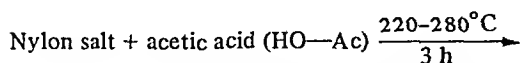
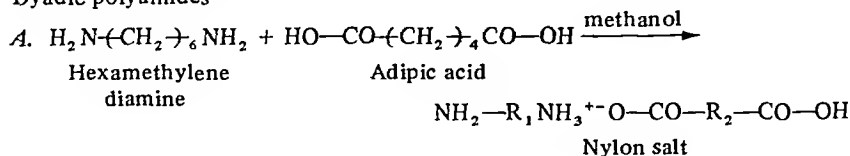
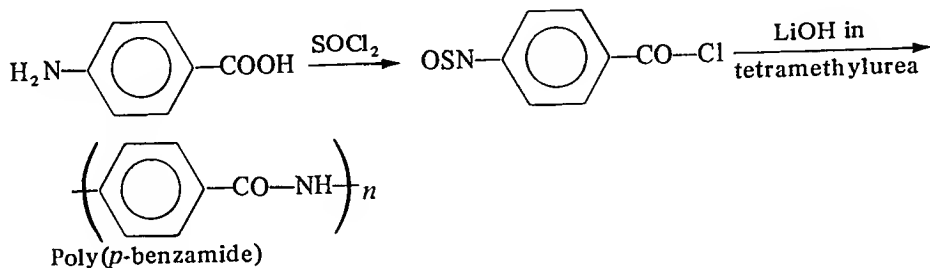
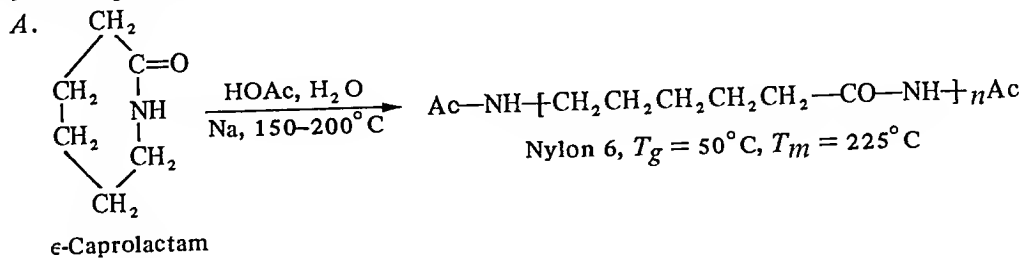
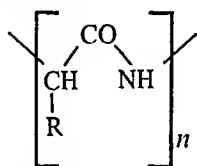


TABLE 14-7
Polyamides and Polyimides (Continued)

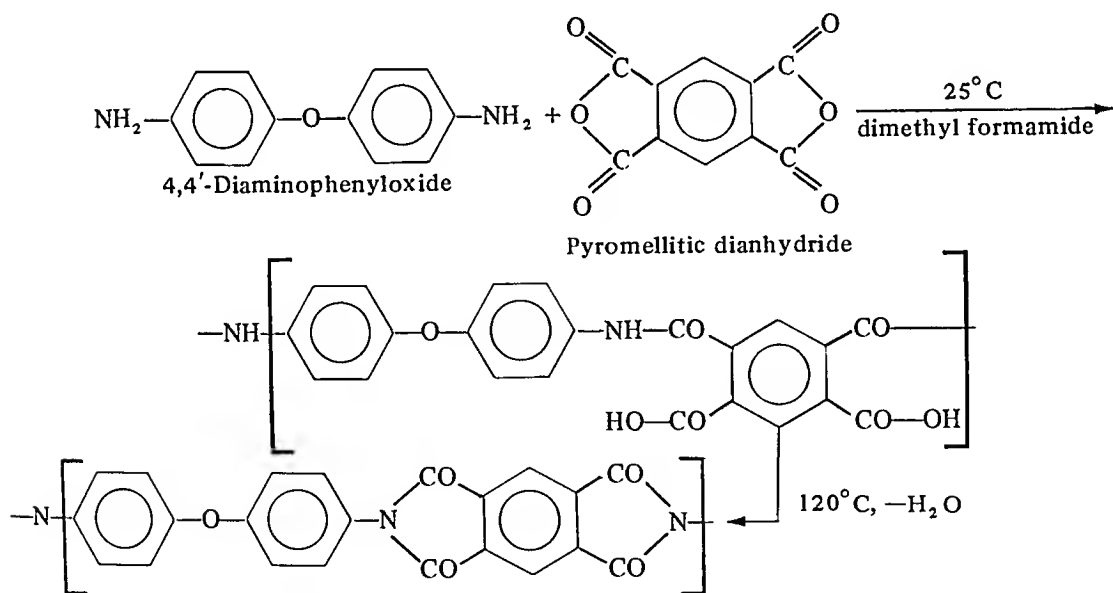
II. Monadic polyamides



B. Proteins



III. Polyimides

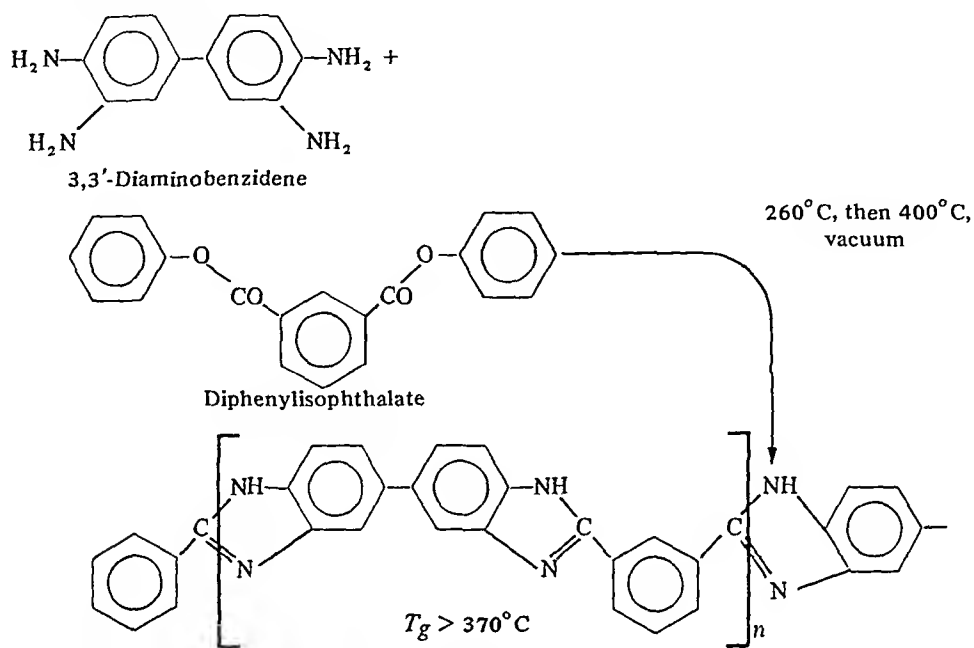


Stable at 420°C (air), 500°C (vacuum).

Tensile strength at 260°C is two-thirds that at 25°C

TABLE 14-7
Polyamides and Polyimides (Continued)

IV. Polybenzimidazoles



have a much higher T_m and could be spun into a useful fiber. Nylon 66, made from a dyad of a diamine and a diacid each with six carbons, was commercialized before 1940 and continues to grow in importance today. Nylon 6, based on the ring scission polymerization of ϵ -caprolactam, was produced in Europe before it was introduced to the United States in the 1950s. The 1960s brought the aromatic nylons and polyimides.

The first step in making dyadic nylons is the formation of a salt of amine and acid (without condensation) (Fig. 14-6). The second step involves actual polycondensation. The salt solution is concentrated to about 75% solids before being charged along with a chain terminator such as acetic acid into an autoclave, where a residence time of several hours and a temperature of up to 280°C yield a polymer with a molecular weight of 12 to 15×10^3 . In one process, continuous polymerization takes place in a coiled-tube reactor. Water vapor escapes as a fast-moving, turbulent core while the nylon melt moves along the wall in laminar flow (Fig. 14-7). In this process, the incoming salt solution is 47% solids and the total residence time is about 1 h at 390 psig (2.7 MPa), 290°C. In a pilot plant unit the coil consisted of 300 ft of $\frac{3}{8}$ -in.-diameter stainless-steel tubing followed by 120 ft of $\frac{1}{4}$ -in.-diameter tubing. A reservoir at the end of the reactor allowed steam to separate and escape. A production rate of 40 lb/h (18 kg/h) is claimed for a unit of this size.

Not all nylons are highly crystalline. The polyamide based on dimerized fatty acids (Table 14-7, 1B) is soluble in common solvents and contains residual

TABLE 14-8
Some Amino Acids Isolated from Proteins [8]

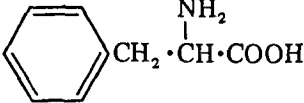
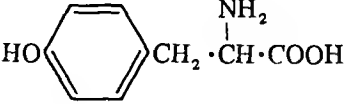
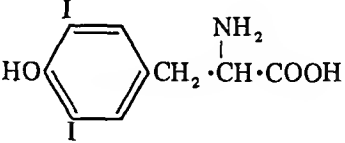
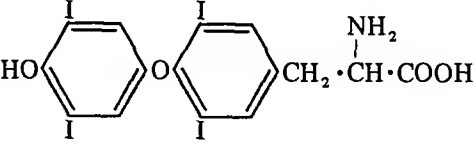
Common name	Systematic name	Structural formula	Discoverer and date
Glycine (glycocoll)	Aminoacetic acid	$\begin{array}{c} \text{NH}_2 \\ \\ \text{HCH} \cdot \text{COOH} \end{array}$	Braconnot 1820
Alanine	α -Aminopropionic acid	$\begin{array}{c} \text{NH}_2 \\ \\ \text{CH}_3 \cdot \text{CH} \cdot \text{COOH} \end{array}$	Strecker 1850
Valine	α -Aminoisovaleric acid	$\begin{array}{c} \text{H}_2\text{C} \quad \text{NH}_2 \\ \diagdown \quad \\ \text{CH}_3 \cdot \text{CH} \cdot \text{CH} \cdot \text{COOH} \end{array}$	Gorup- Besanez 1856
Leucine	α -Aminoisocaproic acid	$\begin{array}{c} \text{H}_3\text{C} \quad \text{NH}_2 \\ \diagdown \quad \\ \text{CH}_3 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{COOH} \end{array}$	Proust 1819
Isoleucine	α -Amino- β -ethyl- β -methyl-propionic acid	$\begin{array}{c} \text{H}_5\text{C}_2 \quad \text{NH}_2 \\ \diagdown \quad \\ \text{CH} \cdot \text{CH} \cdot \text{COOH} \\ \diagup \\ \text{H}_3\text{C} \end{array}$	F. Ehrlich 1903
Serine	α -Amino- β -hydroxy- propionic acid	$\begin{array}{c} \text{OH} \quad \text{NH}_2 \\ \quad \\ \text{CH}_2 \cdot \text{CH} \cdot \text{COOH} \end{array}$	Cramer 1865
Threonine	α -Amino- β -hydroxy- <i>n</i> -butyric acid	$\begin{array}{c} \text{NH}_2 \\ \\ \text{CH}_3 \cdot \text{CH} \cdot \text{CH} \cdot \text{COOH} \\ \\ \text{OH} \end{array}$	Schryver and Buston 1925; Rose et al., 1935
Phenylalanine	α -Amino- β -phenyl- propionic acid		Schulze and Barbieri 1879
Tyrosine	α -Amino- β -(<i>p</i> - hydroxyphenyl) propionic acid		Liebig 1846
Iodogorgoic acid	3,5-Diiodotyrosine		Drechsel 1896
Thyroxine	β -3,5-Diiodo-4- (3',5'-diiodo-4- hydroxy) phenyl- α -aminopropionic acid		Kendall 1915

TABLE 14-8
Some Amino Acids Isolated from Proteins [8] (Continued)

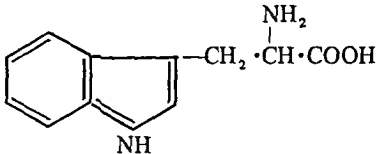
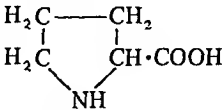
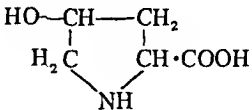
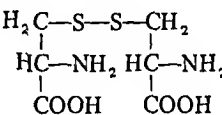
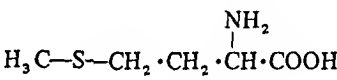
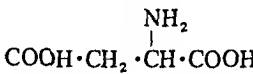
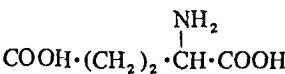
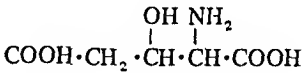
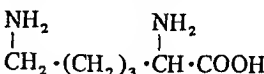
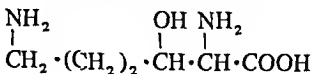
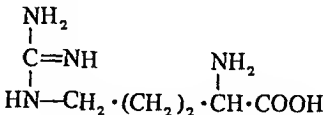
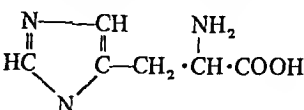
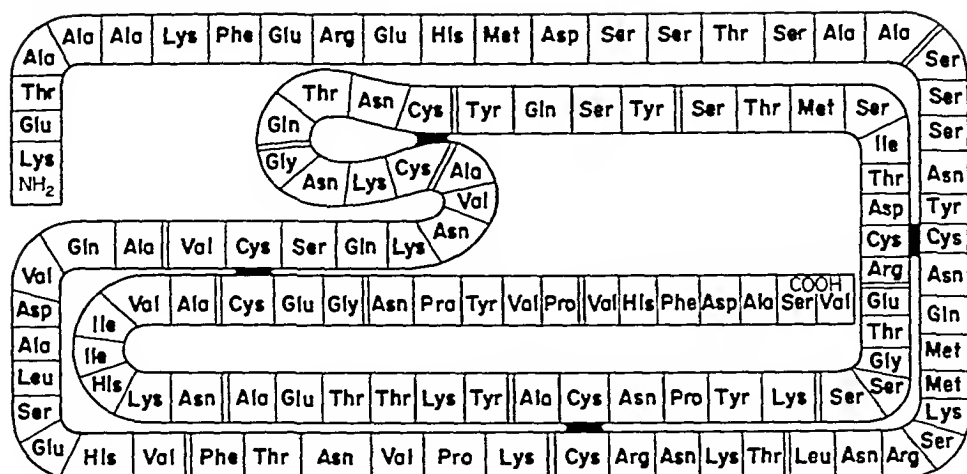
Common name	Systematic name	Structural formula	Discoverer and date
Tryptophan	α -Amino- β -indol-propionic acid		Hopkins and Cole 1901
Proline	Pyrrolidine- α -carboxylic acid		E. Fischer 1901
Hydroxyproline	γ -Hydroxypyrrolidine- α -carboxylic acid		E. Fischer 1901
Cystine	Di-(α -amino- β -thiopropionic acid		Wollaston 1810
Methionine	α -Amino- γ -methylthiol- <i>n</i> -butyric acid		Mueller 1922
Aspartic acid	Aminosuccinic acid		Plisson 1827
Glutamic acid	α -Aminoglutaric acid		Ritthausen 1866
Hydroxyglutamic acid	α -Amino- β -hydroxyglutaric acid		Dakin 1918
Lysine	α - ϵ -Diaminocaproic acid		Drechsel 1889
Hydroxylysine	α - ϵ -Diamino- β -hydroxy- <i>n</i> -caproic acid		Schryver et al. 1925
Arginine	α -Amino- δ -guanidine- <i>n</i> -valeric acid		Schulze and Steiger 1886
Histidine	α -Amino- β -imidazol-propionic acid		Kossel 1896 Hedin 1896

TABLE 14-9
Partial Analysis of Some Proteins [8]

	Egg albumin	Lact- albumin	Serum albumin	Serum globulin	Edesth (hemp)	Glutenin (wheat)	Gliadin (wheat)	Zeln (maize)	Kerathn (wool)	Fibroin (silk)	Gelatn (sperm)	Salmine (salmon)	Casein (cow's milk)	Vitellin (egg yolk)	Insulin (cryst.)	Pepsln (cryst.)
Glycine	0.0	0.4	0.0	3.5	3.8	0.9	0.0	0.0	0.6	40.5	25.5	—	0.5	1.1		
Alanine	2.2	2.4	2.7	2.2	3.6	4.7	2.0	9.8	4.4	25.0	8.7	—	1.9	0.2		
Valine	2.5	3.3	—	—	6.3	0.2	3.4	1.9	2.8	—	0.0	4.3	7.9	2.4		
Leucine and Isoleucine	10.7	14.0	20.0	18.7	14.5	6.0	6.6	25.0	11.5	2.5	7.1	—	9.7	11.0	30.0	
Phenyl- alanine	5.1	1.3	3.1	3.8	3.1	2.0	2.4	7.6	—	11.5	1.4	—	3.9	2.8	+	
Tyrosine	4.2	2.0	4.7	6.7	4.6	4.5	3.4	5.9	4.8	11.0	0.0	—	6.6	5.0	12.2	10.3
Tryptophan	1.3	2.7	0.5	2.3	2.5	1.7	1.1	0.2	1.8	—	0.0	—	2.2	2.5	—	2.2
Threonine	—	—	—	—	—	—	—	—	—	1.5	—	—	3.6	—	2.7	
Glutamic acid	14.0	12.9	7.7	8.2	19.2	25.7	43.7	31.3	12.9	—	5.8	—	21.8	12.2	30.0	18.6
Hydroxy- glutamic acid	1.4	10.0	—	—	—	1.8	2.4	2.5	—	—	0.0	—	10.5			
Aspartic acid	6.1	9.3	3.1	2.5	10.2	2.0	0.8	1.8	2.3	—	3.4	—	4.1	0.5	—	6.8
Proline	4.2	3.8	1.0	2.8	4.1	4.2	13.2	9.0	4.4	1.0	9.5	11.0	9.0	4.0	+	
Hydroxy- proline	—	—	—	—	—	—	—	—	—	—	14.1	—	0.2			
Serine	—	1.8	0.6	—	0.3	0.7	—	1.0	2.9	13.6	0.4	7.8	5.0	—	3.6	
Cystine	1.3	4.3	6.1	1.0	1.0	1.8	—	0.8	13.1	—	0.2	—	0.3	1.2	12.2	1.4
Methionine	4.6	2.6	—	—	2.1	—	2.1	2.3	—	—	—	—	3.4	—	0.0(?)	
Arginine	5.2	3.0	4.8	5.2	15.8	4.7	2.9	1.8	7.8	0.7	8.2	87.4	3.8	7.8	3.2	2.7
Histidine	1.4	2.1	1.2	0.9	2.2	1.8	1.5	0.8	0.7	0.1	1.0	—	2.5	1.2	8.0	0.1
Lysine	6.4	8.8	6.9	6.2	2.2	1.9	0.6	0.0	2.3	0.3	5.9	—	6.0	5.4	2.2	2.1
Ammonia	1.4	1.3	—	—	2.3	4.0	5.2	3.6	—	—	0.4	—	2.3	—	1.7	8.8



The building blocks: 19 amino acids

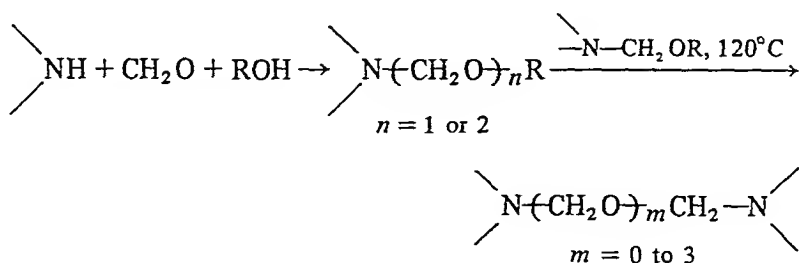
Ala — Alanine	Gln — Glutamine	Leu — Leucine	Ser — Serine
Arg — Arginine	Glu — Glutamic acid	Lys — Lysine	Thr — Threonine
Asn — Asparagine	Gly — Glycine	Met — Methionine	Tyr — Tyrosine
Asp — Aspartic acid	His — Histidine	Phe — Phenylalanine	Val — Valine
Cys — Cysteine	Ile — Isoleucine	Pra — Proline	

COOH—Carboxy group NH₂—Amino group

FIGURE 14-5

The structure of ribonuclease A. The double lines indicate where small units were fused together in one method of synthesis. The second method involved adding monomers one at a time starting from the carboxy end [9].

unsaturation. It is used as a coating material and as a reactive curing agent for epoxy resins in coatings and adhesives. Ordinary nylon 66 is soluble only in highly polar solvents such as 90% formic acid or metacresol. Treatment of nylon with formaldehyde and an alcohol while the polymer is dissolved in 90% formic acid (phosphoric acid is added as a catalyst) results in the *N*-alkylated derivative, which is soluble in methanol and ethanol and can be used in coatings [13]. The coatings can be cross-linked by baking in the presence of an acid (20 min at 120°C with 2% citric acid is typical).



Other commercially available nylons such as nylon 610 (using sebacic acid, HO—CO—(CH₂)₈—CO—OH) are based on aliphatic dyads. The *T_g* and *T_m* can be increased by incorporating cyclic or aromatic structures into the backbone. The

nylons in Table 14-7, IC, can be made by interfacial polymerization (see Sec. 5-3), since the amide formation is rapid between aroyl chlorides and aromatic amines.

Nylon 6 is made by a ring-scission polymerization which results in an equilibrium mixture of high-molecular-weight, linear polymer and cyclic monomer. High-strength fibers require removal of the unreacted monomer. This can be done in

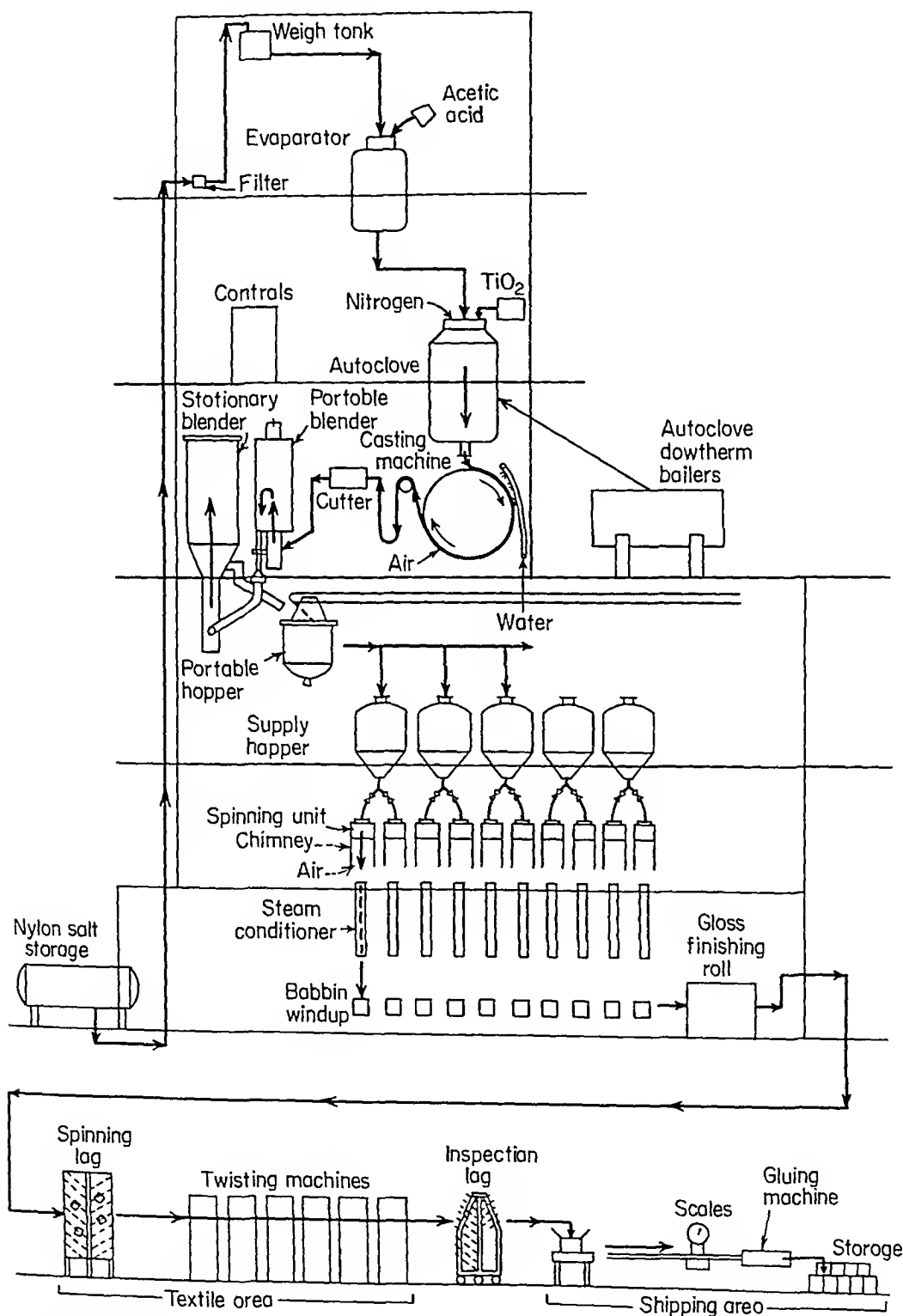


FIGURE 14-6

Nylon 66 production [11].

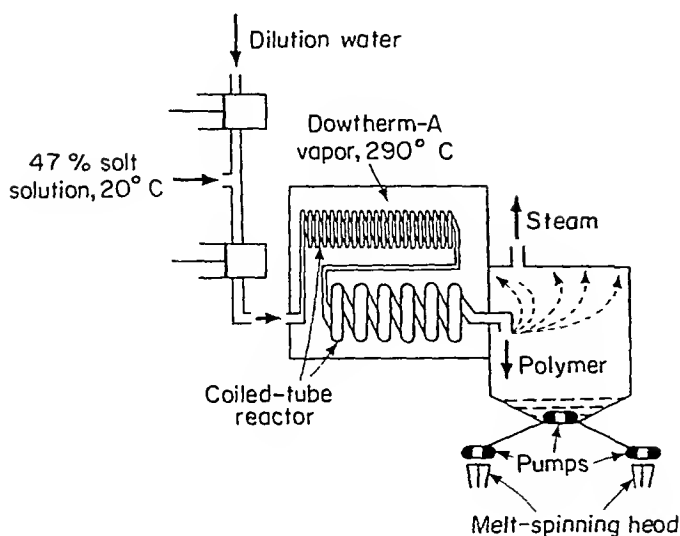


FIGURE 14-7
Coiled-tube reactor for continuous polymerization of nylon 66 [12].

a continuous process (Fig. 14-8) that starts with molten caprolactam. Titanium dioxide can be added at the very start, since it is inert during the reaction and serves only as a delusterant in the final fiber. After a residence time in the reactor of about 18 h at 260°C, the melt viscosity reaches about 100 Pa·s. The unreacted monomer (about 10% of the batch) is removed and recovered in a falling-film evaporator at 260 to 280°C at an absolute pressure of about 0.001 atm.

Large cast pieces of nylon 6 can be produced directly from monomer by using a catalyst such as sodium metal or a Grignard reagent. Much higher molecular weights can be tolerated and less unreacted monomer is left in the molded piece when the temperature is limited to the range between the melting point of ϵ -caprolactam, 72°C, and the melting point of the polymer, 225°C. In one example, *N*-acetyl caprolactam (0.005 mol) and methyl magnesium bromide (0.005 mol) were added to 1 mol of caprolactam at 130°C. The mixture became solid in 4 min. The liquid system can be poured into a mold and converted to the solid *in situ* [15].

The polyimides and polybenzimidazoles (Table 14-7, II and IV) represent attempts to combine chain stiffness with thermal stability. A two-step synthesis is usually required. In the first step a linear, soluble, and fusible polymer is made by forming amide links. At this stage the polymer can be cooled and stored and then later heated and fabricated into a final shape such as a film, fiber, or molded object. In the second step, at a higher temperature than that used in the first step, heterocyclic ring structures are made by intramolecular condensation. While the structures shown in Table 14-7 predominate, there is some intermolecular cross-linking also. At any rate, the materials are nominally thermosetting, since they cannot be formed again by reheating after extensive ring formation. They have the disadvantage of not being easily formed compared to the aromatic polyamides. However, in general, they preserve their strength and flexibility to higher temperatures than can be attained by the true thermoplastics. Commercial polyimide film

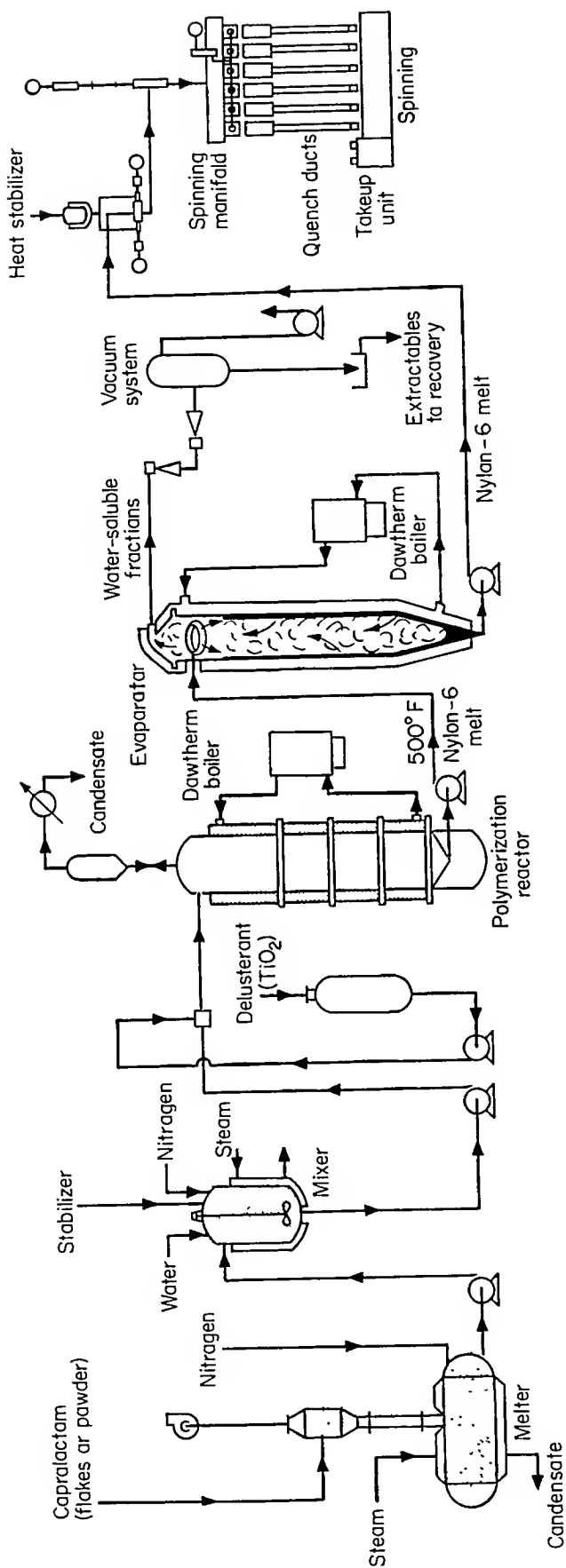


FIGURE 14-8
Production of nylon 6 [14].

Aromatic polyamides (Table 14-7, IC) have been used for flame-resistant garments for firemen and astronauts and as light-weight body-armor for military and law-enforcement agents. In some tests, seven layers of fabric made from an aromatic polyamide were sufficient to protect against the effect of most common handguns. Such a "bullet-proof vest" weighs less than two kilograms. Fiber type, fabric weave, and garment design are all factors in making such a product.

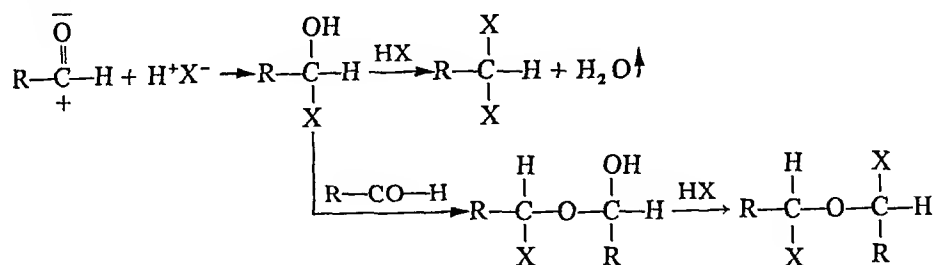
Of the numerous nylons on the market, nylon 66 and nylon 6 (a total of 1.24×10^9 kg) dominated the fiber market in 1979 (Table 14-10). In comparison, the 0.140×10^9 kg going into molded plastics seem like small potatoes. One outlet for nylon fibers, tire cord, consumes about three times as much nylon as do molded goods.

Historians disagree about the birthday of plastics. Some contend that cellulose nitrate in the 1860s started it all, but purists hold out for 1907, when Dr. Leo H. Baekeland patented the resins based on phenol and formaldehyde, an entirely synthetic polymer (Table 14-11). The urea-formaldehyde resins were introduced in the 1930s, opening up the possibility of light colors that were impractical in phenolics. Sterilizable, rugged plastic dinnerware based on melamine resins made a great impact on the market after World War II. The exciting growth of thermoplastics in the 1950s tended to overshadow the thermosets. But in the 1960s it was

[illegible]

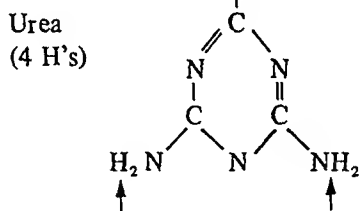
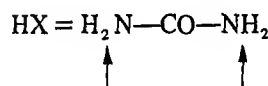
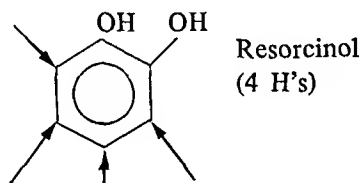
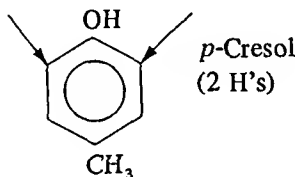
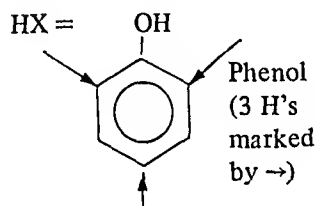
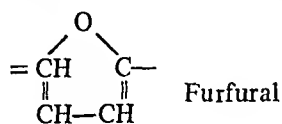
TABLE 14-11
Aldehyde Condensation Products

I. General reaction

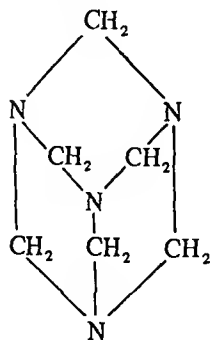


II. Reactants

R = H— Formaldehyde



III. Curative



C₄H₈N₆, Hexamethylenetetramine

found that urea and melamine resins could be used to impart permanent press to cottons and other fabrics. The phenolic resins were found to perform well as ablative materials in reentering space vehicles. Over the intervening years so many markets became important for the aldehyde condensation polymers that no one use can be said to dominate the market for any one polymer. Coatings and adhesives,

laminating adhesives for plywood, bonding agents for grinding wheels and fiberglass filters, and paper-treating agents all claim significant portions of the 1.3×10^9 kg (1978) production of aldehyde condensation polymers.

A typical *one-stage* phenolic resin might be made in a vessel of the type shown in Fig. 14-9. An excess of formaldehyde (as a 40% solution in water) with the phenol and an alkaline catalyst (NH_3 or Na_2CO_3) is refluxed for an hour or so. A charge of 1.5 mol aldehyde per mole of phenol is typical. A branched, water-soluble, hydroxyl-bearing polymer of low molecular weight called a *resole* is formed. Dehydration by heating under a vacuum may take 3 or 4 h. The polymer is removed and cooled. Casting resins, bonding resins, and resins for laminating paper and wood are made this way. The product, when heated with further dehydration, will cross-link completely to give a hard, infusible network like that pictured in Table 4-4.

For a *two-stage* resin, about 0.8 mol formaldehyde per mole of phenol might be used with an acid catalyst (oxalic acid or sulfuric acid is typical). Over a heating period of 2 to 4 h at reflux, the soluble, fusible *novolak* resin forms (Fig. 14-10). Water is removed at temperatures as high as 160°C (higher temperatures than can be tolerated with resoles). The molten, low-molecular-weight polymer is cooled, and the glassy product is crushed, blended with a lubricant and an "activator" and filler, then rapidly mixed on differential rolls. The resultant blend is quickly cooled and

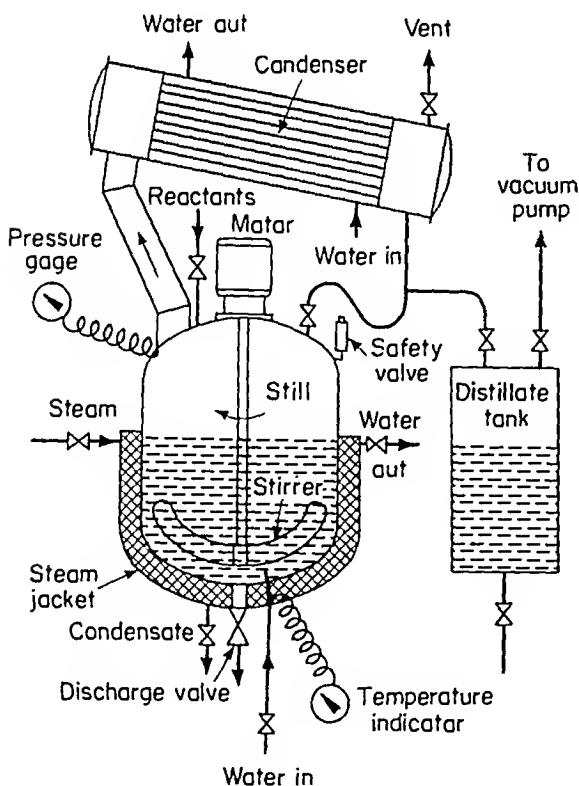


FIGURE 14-9

Reaction vessel for manufacture of phenol-formaldehyde resins [16].

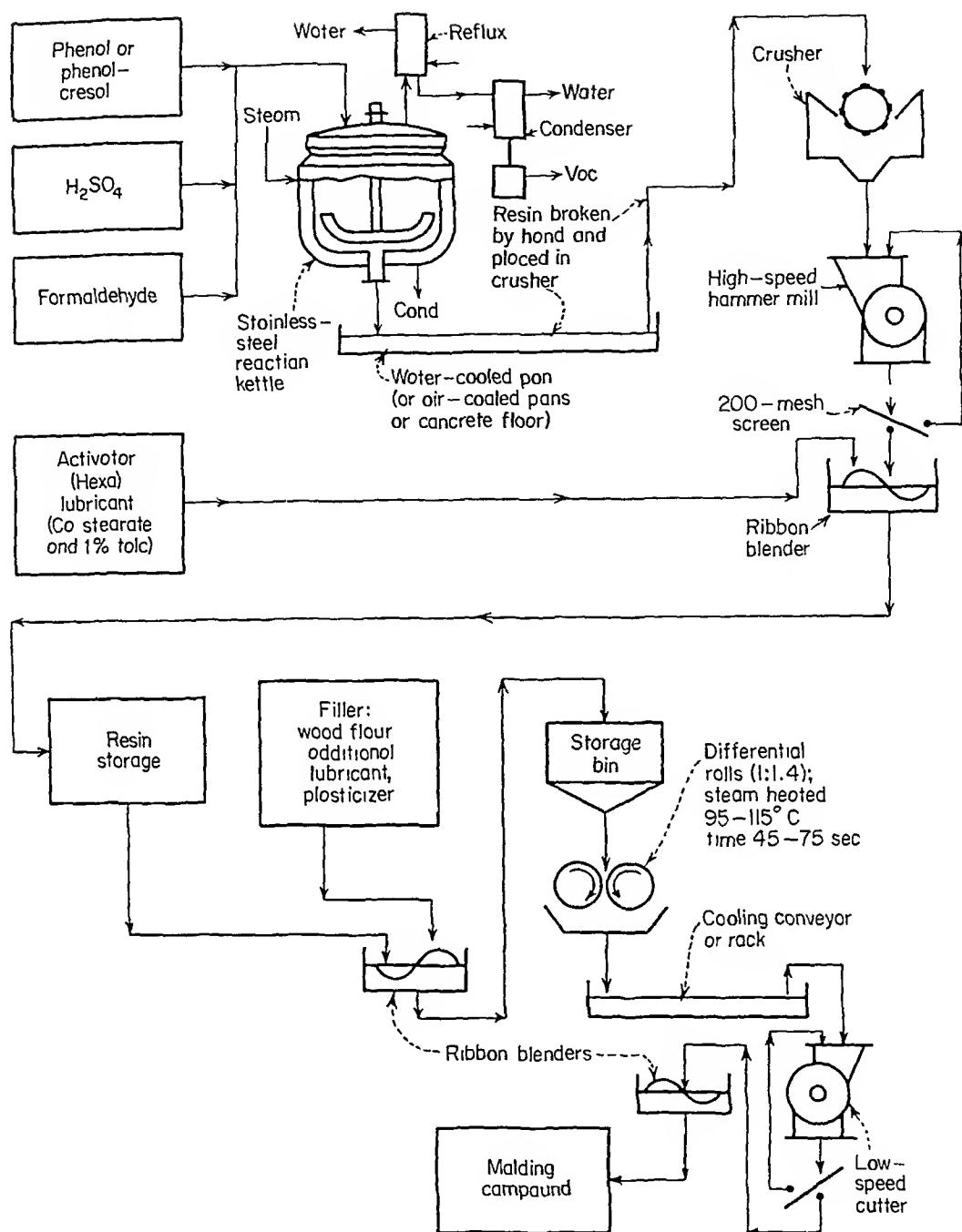


FIGURE 14-10

Flow sheet for phenol-formaldehyde molding powders [17].

made into a molding powder by cutting and blending. The activator is usually hexamethylenetetramine (structure in Table 14-11, III). This compound is the reaction product of 6 mol of formaldehyde and 4 mol of ammonia. When heated in the final molding operation, excess formaldehyde for polymerization is generated together with an alkaline catalyst. In compression molding, a cycle of 10 min at 165°C is usually sufficient to yield a hard, dense, thermoset network. Wood flour (ground wood) is a popular filler, but numerous other fillers, including asbestos, cellulose fibers, and glass fibers, are used.

In considering melamine molding resin production it should be noted that the filler (alpha cellulose in this case) is added to the wet syrup from the reaction kettle without removing water, rather than being mixed with dry resin as in the case of the phenolic resin. The mixture is then dehydrated, ground, mixed, and finally converted into a molding powder. A molar ratio of 2:1 (formaldehyde to melamine) and a pH of 8.6 are maintained until condensation has proceeded to the desired point as evidenced by insolubility of a sample in cold water. To make an unfilled resin for laminating paper, the syrup is spray-dried after reaching the required viscosity. The dried powder is redissolved by the consumer in order to steep his layers of paper.

As with the polyamides, the melamine or urea condensation products can be *N*-alkylated with formaldehyde and an alcohol such as methanol or butanol. The resulting compositions have good solubility in common solvents and are used in textile treatment and in protective coatings.

Use Pattern

As mentioned above, no single use dominates the aldehyde resin market (Table 14-12). Over a period of many years, dozens of minor variations in the resins have been produced. Substitution of furfural for formaldehyde adds ethenic functionality. Phenolic resins have been made into ion-exchange resins by sulfonation and other reactions used with polystyrene resins (see Sec. 13-3).

14-6 POLYMERS BASED ON ISOCYANATE REACTIONS

During World War II, products in all the major categories of Table 14-13 were investigated in Germany. It was not until the 1950s that "urethane" foam was produced in this country on a large scale. Flexible foam continues to be the dominant product, even though many other items are made on a commercial scale.

Foams were discussed in Sec. 12-6. The diols and polyols used usually are polyethers, although polyesters are preferred for some applications such as textile backings because they adhere more readily to the substrates.

TABLE 14-12
Amino and Phenolic Resins—Applications

	Phenolics	Aminos
Abrasives	x	
Fibrous and granulated wood binder	x	x
Foundry and shell moldings	x	
Brake linings, etc.	x	
Laminating resins	x	x
Molding materials	x	x
Plywood	x	x
Protective coatings	x	x
Thermal insulation	x	
Paper treating	—	x
Textile treating	—	x

TABLE 14-13
Isocyanate Reaction Polymers

I. Products

A. Foams

Flexible or rigid depending mainly on branched structure of diol
 "Prepolymer" or "one-shot"
 Polyester or polyether diol

B. Elastomers

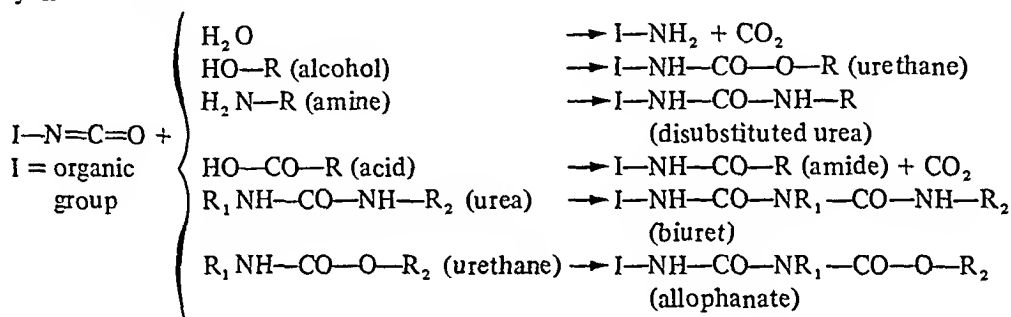
Cast
 Thermoplastic
 Millable, vulcanizable

C. Fibers

Nylon-like
 Spandex, elastic

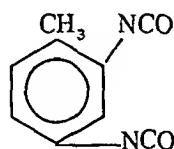
D. Adhesives and coatings

II. Isocyanate reactions

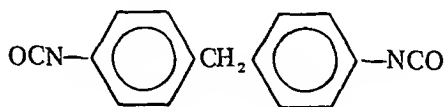


III. Commercial diisocyanates

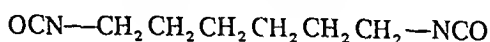
Tolylene-2,4-diisocyanate (TDI), often used as mixture with 2,6 isomer



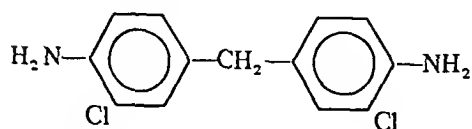
Methylene-bis(4)phenyl isocyanate (MDI)



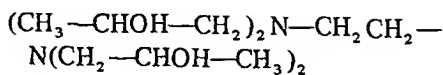
Hexamethylene diisocyanate (HDI)



IV. Chain-extending agents

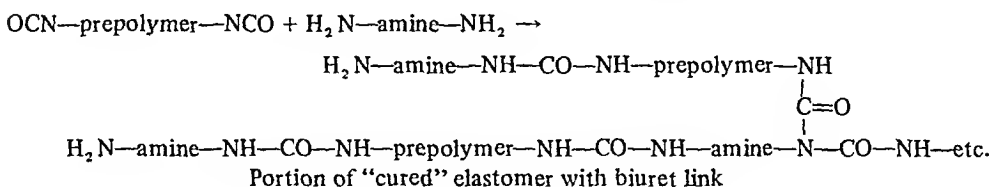


4,4'-methylene-bis-(2-chloro aniline)

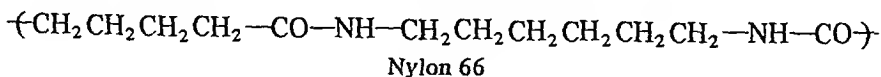
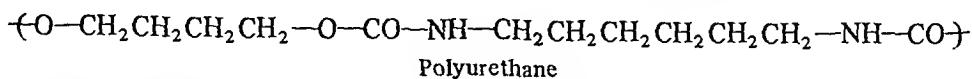


N,N,N',N'-Tetrakis(2-hydroxypropyl) ethylene diamine

TABLE 14-13
Isocyanate Reaction Polymers (Continued)

$$\begin{array}{ccc} \text{HO—polyester—OH} + \text{I(NCO)}_2 & \rightarrow & \text{OCN(I—NHCO—O—polyester—O—CONH)}_n\text{I—NCO} \\ \text{Diol} & \text{Diisocyanate} & \text{Isocyanate-terminated prepolymer} \\ & & n = 2 \text{ to } 5 \end{array}$$


One nylon-like fiber has been produced in Germany for some time based on 1,4-butanediol and hexamethylene diisocyanate. The structure resembles nylon 66 except for two additional oxygens per repeating dyad. Their properties are similar except that (the urethane has lower water adsorption and somewhat better electrical and mechanical stability on aging.) However, the urethane apparently has not shown



sufficient advantage to warrant introduction in the United States.

Elastic fibers that are at least 85% by weight polyurethanes have the generic name spandex. As a primitive example, one could take the thermoplastic elastomer mentioned above, dissolve it in dimethyl formamide, and extrude it through a spinneret into an aqueous bath, which will cause the polymer to precipitate, the dimethyl formamide dissolving in the water. The fibers may be dried, drawn, and put through all the processes associated with fiber production (see Sec. 12-5). One commercial fiber appears to be the result of chain-extending with a diamine, a prepolymer based on MDI and poly(tetrahydrofuran). The fibers find use in foundation garments, surgical hose, and swimsuits. They compete here with natural rubber thread made by slitting extruded, vulcanized rubber sheets.

In coatings and adhesives, isocyanates may be used as reactive species at room temperature, or by modification, at high temperatures. Most "urethane" varnishes, however, are probably solutions of alkyd resins modified by reaction of free hydroxyl groups with diisocyanates.)

Use Pattern

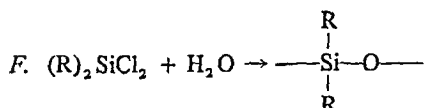
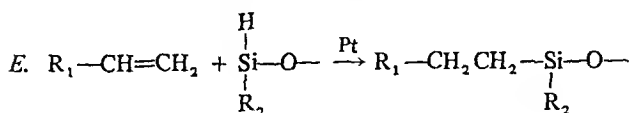
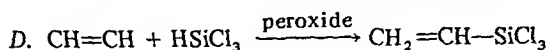
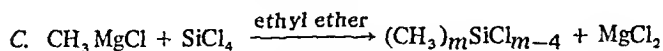
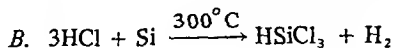
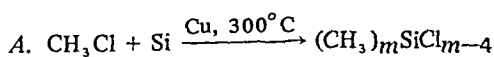
Except for the nylonlike urethane fiber, the isocyanate polymers are characterized by a segmented structure in which the rather polar urethane groups act as cross-links and the connecting chains are varied in stiffness and polarity depending on the application. In the elastomeric and coatings applications, the one property most often cited as being superior for polyurethanes over other materials is abrasion resistance. Pneumatic tires said to outlast conventional rubber tires have been constructed from unfilled cast elastomers. Other properties such as traction and cost presumably have kept them from becoming commercially available. Solid tires for fork-lift trucks are made from cast polyurethanes, especially for locations where oil resistance is a prerequisite. By far the major product group for the isocyanate-based polymers has been flexible foams for bedding, furniture, and rug underlays. In 1978, 608×10^9 kg of flexible foams were used, while another 232×10^9 kg of rigid foams went into building insulation, other forms of insulation, and furniture. Reaction injection molding (RIM, see Sec. 12-6, Molding), which produces parts with densities about 80% of the corresponding solid materials, is growing in importance (40×10^9 kg in 1978).

14-7 SILICONES

The need during World War II for a heat-resistant, flexible electrical insulating material accelerated development of the silicones on the basis of research previously done by Kipping (England) and Hyde (U.S.). The Dow Corning Corporation (1943) and General Electric Company (1946) were the first producers of fluids and rubber based on silicones. Union Carbide Corporation (1956) had supplied silicon metal to silicone producers for some time before entering production of polymers. Recently, Stauffer Chemical Company also began production. In addition to the heat resistance associated with silicones, the low-temperature flexibility inherent in the Si—O bond (Sec. 2-2) and the low surface tension of silicones suit them for many applications despite their relatively high cost. Most silicone monomers start with reactions of silicon metal or SiCl_4 derived from $\text{Cl}_2 + \text{SiC}$. Originally, the Grignard

TABLE 14-14
Silicones

I. Monomer production



II. Product classes

A. Fluids

B. Rubber

Dimethyl siloxane

Methyl, phenyl copolymer

Fluoromethyl siloxane

C. Resins

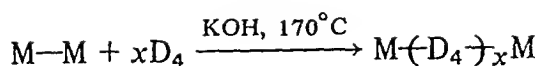
D. Surfactants

E. Coupling agents

synthesis was widely used commercially (Table 14-14, IC). The "direct" reaction of alkyl and aryl chlorides with silicon metal is favored today (Table 14-14, IA, B). In either case, monomers of variable functionality are formed and must be separated prior to hydrolysis (Table 14-14, IF). Since a monochlorotrialkyl silane, ClSiR_3 , has only one hydrolyzable group, we can abbreviate it in the hydrolyzed form as M—. Because the free hydroxyls are not stable in general, the product of hydrolysis is $\text{R}_3\text{Si}-\text{O}-\text{SiR}_3$, abbreviated M—M. The difunctional group, R_2SiO , is abbreviated by D, $\text{RSiO}_{1.5}$ by T, and SiO_2 by Q.

A peculiarity of the hydrolysis of dichlorosilanes is the formation of many ring structures. In addition to the cyclic tetramer, D_4 , simple mixing of $(\text{CH}_3)_2\text{SiCl}_2$ with alkaline water leads to appreciable quantities of D_3 , D_5 , D_6 , etc. Vapor-liquid chromatography is able to confirm the presence in hydrolyzate of rings up to D_{40} . Production of many silicone compounds starts with redistilled hydrolyzate, which is predominantly D_4 .

By heating D_4 together with the appropriate amount of M—M in the presence of a strong base (KOH) or acid (H_2SO_4), an equilibrium composition may be reached in which the molecular weight of the linear portion is regulated by the amount of end groups (M) added. Neutralization of catalyst and vacuum distillation



can give a linear fluid with most of the cyclic species removed. The relationship between melt viscosity and molecular size is shown in Fig. 7-7. [Dimethyl siloxanes with viscosities at room temperature of up to 100,000 centistokes are used as lubricants, antifoaming agents, and additives for cosmetics, pharmaceutical preparations, and hundreds of other consumer products. An interesting feature of dimethyl siloxanes is their low viscosity-temperature coefficient [VTC, Eq. (14-1)] compared with that of hydrocarbon lubricants.]

$$\text{VTC} = 1 - \frac{\text{viscosity at } 210^\circ\text{F}}{\text{viscosity at } 100^\circ\text{F}} \quad (14-1)$$

The effect is lost, however, when phenyl, ethyl, or other groups are substituted for methyl (Table 14-15). Only the substitution of hydrogen for methyl lowers the VTC.

When D_4 is heated to 170°C with a small amount of KOH and no added end blocker, high-molecular-weight gums are produced. The molecular weight distribution corresponds roughly to the "most probable" distribution (Sec. 6-2) for the linear portion. The cyclic species form a separate distribution. Gel permeation chromatography (Sec. 6-4) shows the initial distribution and the distribution after neutralization of catalyst and vacuum stripping (Fig. 14-11). No redistribution seems to occur in the linear portion, and most of the cyclic species are removed. [Most commercial gums are copolymers with 0.2 to 0.6% vinylmethylsiloxane. The vinyl group provides a preferential cross-linking site with peroxides.] The tensile strength of unfilled, cross-linked silicone rubber is only a few hundred pounds per square inch at best. Fillers, especially finely divided silica, raise this into the range of 1200 to 2000 psi (8 to 14 MPa). Even with the vinyl comonomer and cross-linking,

TABLE 14-15
Temperature Dependence of Viscosity for Polysiloxanes [18]

Substituents:	Viscosity at 25°C, cs*	VTC [Eq. (14-1)]
Dimethyl (M—M)	0.65	0.31
Dimethyl (MD ₃ M)	2.0	0.48
Dimethyl	10	0.57
Dimethyl	10 ²	0.60
Dimethyl	10 ³	0.62
Dimethyl	10 ⁴	0.61
Dimethyl	10 ⁵	0.61
Methylphenyl	482	0.88
Methylethyl	1300	0.71
Diethyl	800	0.90
Methylhydrogen	25	0.50
Mineral oil (typical)	110	0.91

*1 cs = 1 mPa·s divided by density (g/cm³).

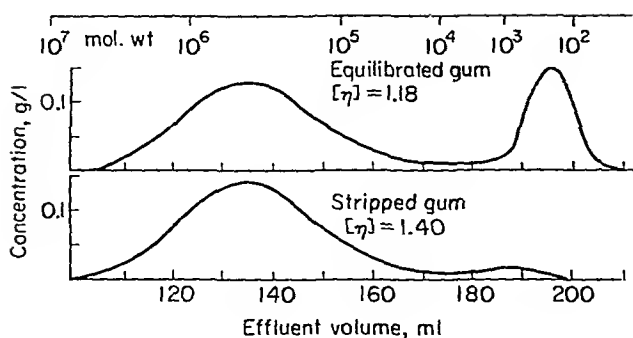
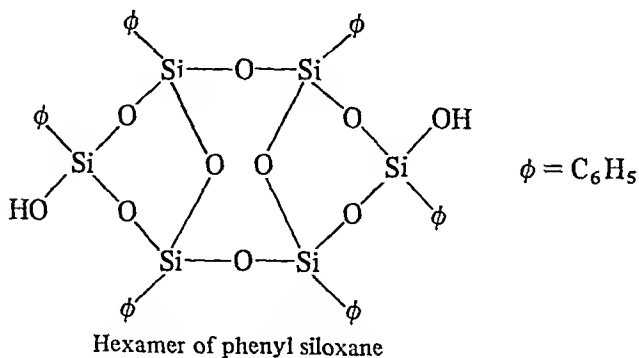


FIGURE 14-11

Gel permeation chromatographs of equilibrated and vacuum-stripped dimethyl siloxane gums [19].

dimethyl siloxanes become stiff at -54°C because of crystallization. The stiffening temperature is brought close to the glass-transition temperature (-110°C) by copolymerization with phenylmethyl or diphenyl siloxane (see Sec. 3-5). [Some silicone fluids with hydrolyzable or reactive end groups have been compounded with fillers and catalysts to make RTV (room-temperature vulcanizing) rubber.] An example of a one-package system that converts to a rubber on exposure to moist air was given in Sec. 12-4.

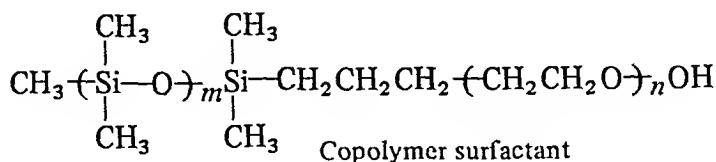
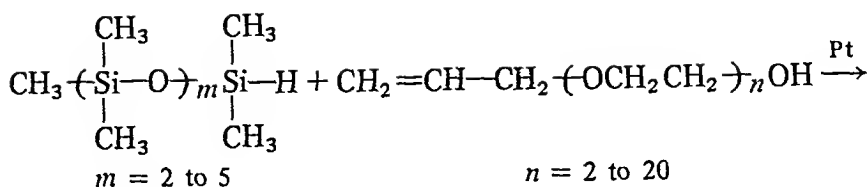
Silicone resins for coatings resemble phenol-formaldehyde polymers in that polymerization takes place in two stages. A trifunctional monomer such as phenyltrichlorosilane may be hydrolyzed to the relatively stable hexamer (and related structures modified by comonomers for better solubility). This compound



when heated alone or with carboxylic acids and esters will undergo further condensation and rearrangement to give heat-stable, network polymers.

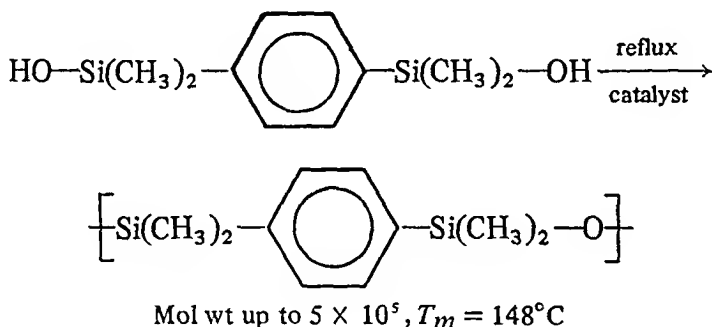
[Surfactants based on block copolymers of dimethylsiloxane with poly(ethylene oxide) are unique in regulating the cell size in polyurethane foams. One route to such polymers uses reaction 1E, Table 14-14, between a polysiloxane and an allyl ether of polyethylene oxide [20]. Increasing the silicone content makes the surfactant more lipophilic, while increasing the poly(ethylene oxide) content makes it more hydrophilic.]

The coupling agents used to change the surfaces of silica and glass fillers (Sec. 9-8) are substituted alkoxy silanes in monomeric form. They may polymerize

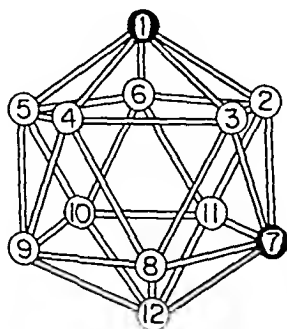


on the surface of the filler, or they can be copolymerized with other organic monomers.

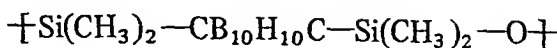
The incorporation of bulky groups into the silicone chain would be expected to raise T_m and T_g . Attempts have been made to do this without sacrificing the high-temperature stability of the silicones. One such material is *p*-bis(dimethylhydroxysilyl) benzene made from *p*-dibromobenzene and $(\text{CH}_3)_2\text{SiCl}_2$ by the Grignard reaction. Polymerization is carried out by refluxing the monomer in benzene with an amine salt acting as a catalyst (*n*-hexylamine 2-ethylhexoate) [21].



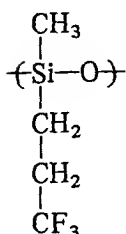
Copolymers with dimethylsiloxane are also possible. A more complicated structure results when *m*-carborane is put in place of the phenylene group. [Thermoplastic



m-Carborane, $\text{C}_2\text{B}_{10}\text{H}_{12}$



resins have been offered on a limited basis, which may be copolymers of carborane with diphenyl siloxane) with $T_m = 235$ to 255°C . Copolymers with dimethylsiloxane also are offered [22]. [Fluorosilicone elastomers can be based on trifluoropropyl-methyl siloxane:



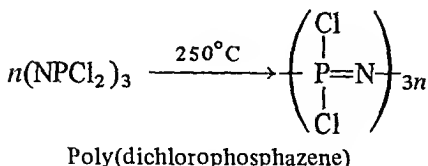
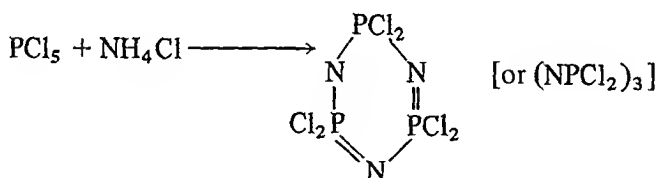
Such elastomers have some of the solvent resistance associated with fluorocarbon polymers. It would seem that a more highly fluorinated monomer would be better. Unfortunately, fluorine on carbons next to or one carbon away from silicon generally lead to thermal or hydrolytic instability [23].

Use Pattern

[It was pointed out above that silicone fluids are used as additives in many products. Their use alone is limited; high-temperature laboratory baths and special lubricants are examples. Silicone rubber and surfactants also find large markets.] A 20×10^9 kg/year market for silicone rubber may seem trivial on a weight basis, but it must be remembered that silicone rubber sells for about 20 times the price of styrene-butadiene rubber.

14-8 POLYPHOSHAZENES

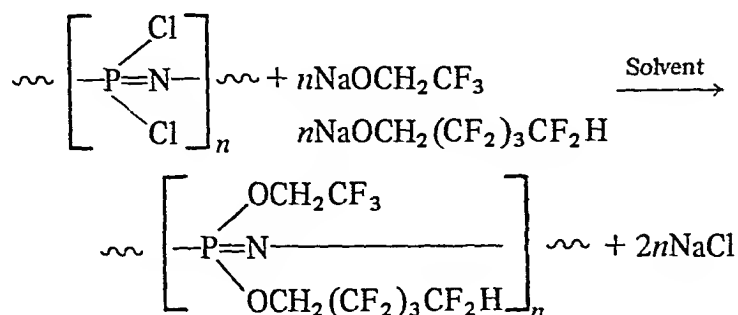
Polymers with the $-\text{P}=\text{N}-$ backbone were produced as long ago as the 1890s. Cyclic phosphonitrilic chloride (which is made from PCl_5 and NH_4Cl) is opened by ring-scission polymerization. A cross-linked version of this “inorganic rubber” was



described by Stokes in 1895 [24, 25]. However, moisture, even atmospheric moisture, soon hydrolyzes this polymer to a brittle material. In the 1960s and 1970s preparation of the dichloropolymer was made reproducible so that it could be used as a precursor for various derivatives. The polymerization of the cyclic trimer proceeds at about 250 to 270°C in a vacuum over a period of 20 to 40 h with reflux. Precipitation of the polymer in hexane or pentane leaves unreacted trimer and some other low molecular weight species in solution. Yields may range from 15 to 75%.

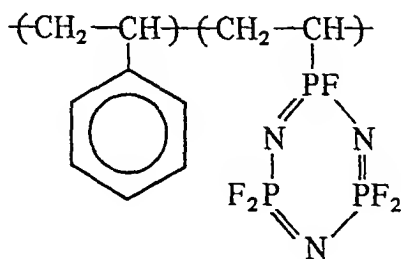
The chlorine atoms on the backbone of the polymer may be replaced by

organic groups such as alkoxy, aryloxy, or amino groups. Most of these derivative polymers do not exhibit the hydrolytic instability of the parent polymer. In order to carry out the substitution, the chlorine-bearing polymer is added dropwise to a solution containing sodium alkoxide, or aryloxy in a solvent such as tetrahydrofuran or benzene. A commercial rubber (PNF, Firestone Tire and Rubber Co.) is based on alkoxides of trifluoroethyl alcohol or heptafluoroisobutyl alcohol [26].



The product is referred to as a phosphonitrilic fluoroelastomer, a "semiorganic" rubber. The useful range is from the T_g of about -68°C up to about 175°C . PNF can be cross-linked by peroxides, sulfur, or high-energy electrons. The outstanding properties of the rubber are excellent oil and fuel resistance, good dynamic properties, and good abrasion resistance. Disadvantages are water resistance that is only fairly good, and a price higher than that of fluorosilicones.

Numerous other derivatives have been reported in the literature. A few examples are tabulated (Table 14-16). In addition to those with phosphazene in the backbone, some contain $-\text{P}=\text{N}-$ in side groups. The reaction of styrene with a vinyl-substituted trimer gives a copolymer that is flame-retardant in a standard test [27].



14-9 ENGINEERING RESINS AND HIGH-PERFORMANCE POLYMERS

In industrial practice, polymer categories may be based on a variety of considerations. Producers of polymers may well use a compositional basis like the one used in the various sections of the previous chapter and this one. Raw materials and techniques for many products may be common to one such group. However, users of polymers often create categories by performance properties such as those summarized in Sec. 10-1. Within a major industry, polymers compete on a price and performance basis. As an example, in the rubber industry one can differentiate

TABLE 14-16
Some Polyorganophosphazenes [25]

Repeat group in compound	T_g , °C	Solvent
—N=PCl ₂ —	-63	Benzene
—N=P(OCH ₃) ₂ —	-76	Methanol
—N=P(OCH ₂ CH ₃) ₂ —	-84	Alcohols
—N=P(OCH ₂ CF ₃) ₂ —	-66	Ketones
—N=P(OC ₆ H ₅) ₂ —	-8	Benzene
—N=P(NH—C ₆ H ₅) ₂ —	91	Benzene
—N=P(N(CH ₃) ₂) ₂ —	-4	Aqueous acid
—N=P(NC ₅ H ₁₀) ₂ —	19	Benzene

among general purpose rubbers (for tires, wire and cable insulation), specialty rubbers (oil-resistant, ozone-resistant, heat-resistant), and thermoplastic elastomers (which need no covalent cross-linking step).

The term *engineering resin* is used to designate a group of heterochain thermoplastics that can compete with some die-cast metals such as zinc, aluminum, and magnesium in plumbing parts, hardware, and automotive parts. Most of these resins (polymers) sell at two to four times the price of the large-volume olefin, vinyl chloride, and styrene polymers. Injection molding is the major fabrication technique used. The polymers usually included and the volume of sales in 1979 are shown in Table 14-17. All the polymers can be used without reinforcement, but glass fibers or mineral reinforcement generally improve dimensional stability at elevated temperatures (see Table 9-2). The flexural modulus and tensile strength as function of temperature of most of these materials are included in Figs. 14-12 and 14-13.

As a group, *high-performance plastics* have been used where high strength or dimensional stability is required at high temperatures. The space exploration program and high-speed aircraft for military applications have been the primary consumers for these materials. Just as *engineering resins* cost more than general-purpose polymers, high-performance plastics are often even more costly. A representative list (Table 14-18) indicates polymers that were available in the mid-1970s. Except for the fluorocarbons, all are heterochain polymers. Several are included in Figs. 14-12 and 14-13. As with most molded plastics, reinforcement enhances high-temperature stability. Glass, boron, or graphite fibers may be used as well as

TABLE 14-17
Sales of Engineering Resins, kg × 10⁻⁶, 1979 [28]

Polymer	Sales
Nylon 66	140
Polycarbonate	109
Poly(phenylene oxide)-polystyrene blends	68
Acetal	48
Poly(butylene terephthalate), "thermoplastic polyester"	26
Polysulfone (estimated)	5

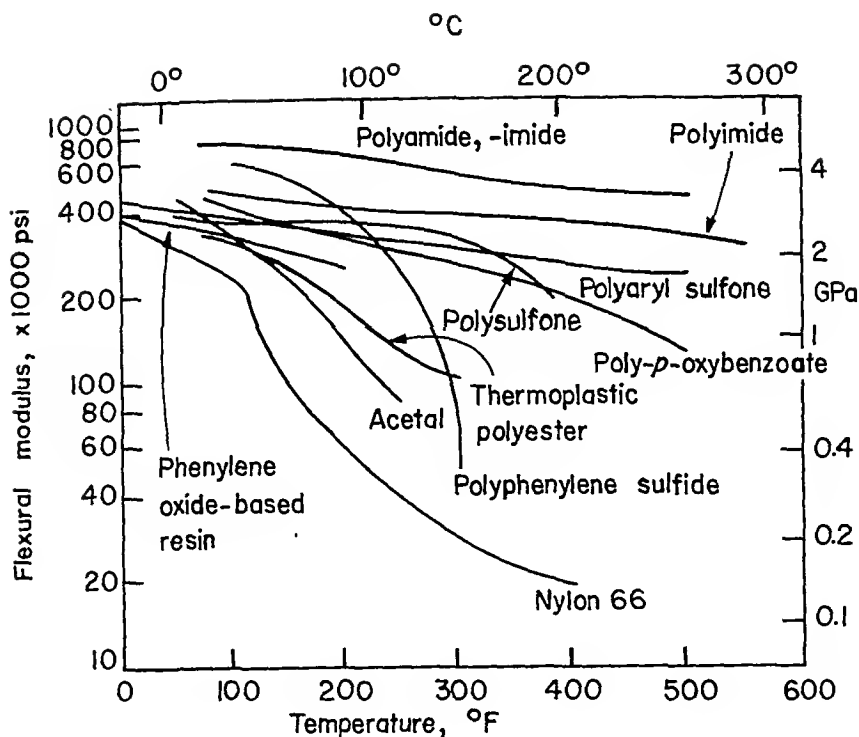


FIGURE 14-12
Flexural modulus of selected molding resins (unreinforced) [29].

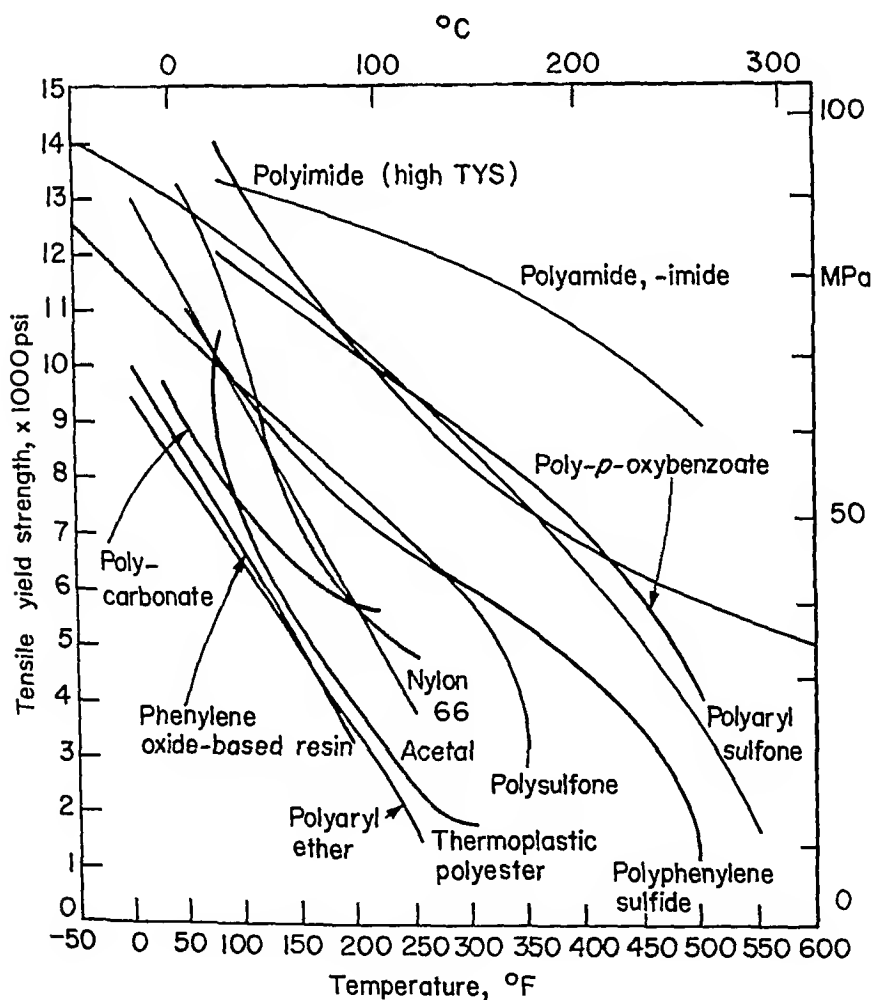


FIGURE 14-13
Tensile yield strength of selected molding resins (unreinforced) [29].

TABLE 14-18
Properties of Some High Performance Plastics* [30]

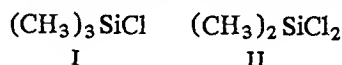
	Tensile strength, MPa	Flexural modulus, GPa	Heat deflection temperature, °C (at 1.8 MPa)	Continuous use temperature, °C
Polyimide				
Thermoplastic	118	3.3	132 to 138	290
Thermoset	62 to 90	—	over 245	—
Thermoset, filled	19 to 39	22	290 to 350	260
Poly(amide-imide)				
Unfilled	92	5	280	290
Filled	78 to 90	5 to 8	285 to 295	290
Polyarylsulfone	90	2.7	—	260
Aromatic polyester	17	7.1	—	—
Aromatic copolyester	70	3.1	over 315	300
Aromatic polyamide	115	4.4	—	—
Polyphenylene sulfide				
Unfilled	70	4.1	137	205 to 260
Filled	145	15	over 215	205 to 260
Silicone resin, filled	25 to 45	7 to 17	over 480	over 315
Poly(tetrafluoroethylene)	15 to 35	—	—	260
Epoxy (mineral-filled)	70 to 140	17 to 30	120 to 260	—
Phenolic (glass-fiber-filled)	35 to 125	14 to 23	150 to 315	—

*Unfilled unless designated otherwise.

mineral fillers. Unlike the category of engineering resins, the high-performance plastics include thermosets such as the silicone molding resins and some polyimides.

PROBLEMS

- 14-1. How many grams of I and II are needed to make 100 g of a poly(dimethyl siloxane) oil with $M_n \approx 10,000$?



- 14-2. Explain why 2,6-dimethyl phenol gives a high-molecular-weight polymer when oxidized but only a low-molecular-weight material with formaldehyde.
- 14-3. In the "equilibration" polymerization of tetrahydrofuran, how can residual monomer be removed without depolymerizing the linear polyether?
- 14-4. What polymers make use of bisphenol A? What properties does it contribute to the polymers?
- 14-5. A fabricated sample of "cast unsaturated polyester" has the following properties:
- It becomes somewhat less stiff at 100°C.
 - It does not flow, even at 300°C.
 - It becomes somewhat weaker on soaking in hot, dilute sodium hydroxide.

Explain how each of these properties is related to the chemical structure of the sample.

- 14-6. Both propylene oxide and styrene oxide can be polymerized to give isotactic polymers that can crystallize.
- Write formulas for the two polymers.
 - Identify the asymmetric carbons.
 - Which of the two polymers would you expect to have the highest T_g ? Why?
- 14-7. Why are most of the new thermoplastics with high heat distortion temperatures heterochain polymers rather than carbon chain polymers? Why is not ring-scission polymerization used more often for them?
- 14-8. In a certain country with an "emerging" economy, a governmental decision has been made to establish a polymer industry based on native resources. No oil refineries or coal tar operations exist. Cotton (pure cellulose) and sugar are the major raw materials. In addition, electrolytic processes can be used, since hydroelectric power abounds. Your first step is to set up plants to produce from sugar, sequentially: ethyl alcohol, acetic acid, and butadiene. From electrolysis you now have NaOH, Cl_2 , HCN, and HCl. Sulfuric and nitric acids are also produced locally.

Outline the steps necessary to establish consumer-product plants for (include reactions where possible):

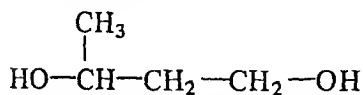
Cellulose acetate film

cis-Polybutadiene rubber (to be used in tires)

Nylon 66 (fibers and molding compound)

(Where you have to import materials, say so.)

Outline briefly the feasibility of producing at least two other polymers and give some idea of where they might be useful. Remember that an intermediate in butadiene production can be



$\text{CH}_3\text{CH}_2\text{Cl}$ is possible, too.

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15

ANALYSIS AND IDENTIFICATION OF POLYMERS

15-1 THE PURPOSE OF POLYMER ANALYSIS

There are a variety of situations that call for the identification of polymers. A customer wishes to paint or glue an item or to use an object in a novel environment. It may be awkward or impossible to obtain the composition from the supplier. In another common case, it may simply be detective work to find a chemical reason why a competitor's product behaves differently than your own. Contaminants in fabrication plants can be very hard to trace. For example, a small amount of a highly unsaturated polymer, such as natural rubber, can prevent the proper cross-linking of a large amount of a more saturated material, such as butyl or EPDM rubber. Of course, many of the tests described as useful in identification are also run routinely as quality controls on known polymers. While infrared spectroscopy is extremely helpful as an identification tool, it is also applied to the measurement of crystallinity and branching in some polymers (notably polyethylene). Physical testing, molecular weight determination, and electrical testing have been discussed previously. The larger polymer producers perform almost all of these tests routinely. The smaller, more specialized laboratories of many fabricators and consumers may not possess all of the instruments needed for these tests. Independent laboratories will perform them on a consulting basis. Where the instruments are expensive or the test method is quite involved, recourse to independent laboratories may be wise.

15-2 INFRARED AND ULTRAVIOLET SPECTROSCOPY

The atoms constituting a molecule are in constant vibration. When the number of atoms in a molecule exceeds 10 or so, the number of possible modes of vibration becomes very large. Fortunately, many frequencies are characteristic of localized bonds. Thus the absorption of light by the stretching of the C—H bond almost always

occurs at frequencies between 2880 and 2900 cm^{-1} . Most infrared spectrophotometers use a glowing light source to provide light with wavelengths from 2.5 to about 15 μm . An alternative system of nomenclature that is popular refers to the reciprocal of wavelength as *wave number* or frequency. A wavelength of 2.5 μm corresponds to a wave number or frequency of 4000 cm^{-1} , 10 μm is equivalent to 1000 cm^{-1} , and so on. A rotating prism or diffraction grating breaks up the light from the source into a spectrum from which various wavelengths are progressively isolated with the aid of filters. A programmed slit compensates for the varying intensity of the source at different wavelengths.

The sample may be a thin unsupported film (usually about 0.001 in thick), a film evaporated on a nonabsorbing substrate such as NaCl, a solution held in a non-absorbing cell (often made of NaCl), a pressed, clear wafer of the material to be analyzed mixed with KBr powder, or a mull of the material with a heavy paraffin oil held between NaCl flats. Other alkali and alkaline-earth halides are used as substrates. Water and alcohols are not used as solvents generally, because they absorb strongly in the infrared region and may corrode the substrates.

In a double-beam instrument the absorption by H_2O and CO_2 vapors is canceled out. By using matched cells in such a machine, one can also compensate for the solvent. It must be remembered that even with compensation, high absorption by the solvent in both cells still reduces the sensitivity of the method at that particular frequency.

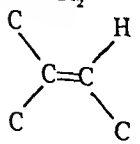
The positions of some characteristic absorption bands are summarized in Table 15-1. Although these are valuable in analyzing spectra, we can often learn much by regarding the entire spectrum as a kind of *fingerprint*. In this way we can identify the more common homopolymers rapidly by simple comparison with standard spectra. Copolymers, terpolymers, and mixtures introduce complications, although the spectra may be simply additive. Some bands are shifted by changes in environment. The OH and NH bands are moved by hydrogen bonding. In fact the shift of the OD band in deuterated methanol when it is mixed with another liquid is used as a measure of hydrogen bonding in classifying solubility and swelling data (Sec. 2-5).

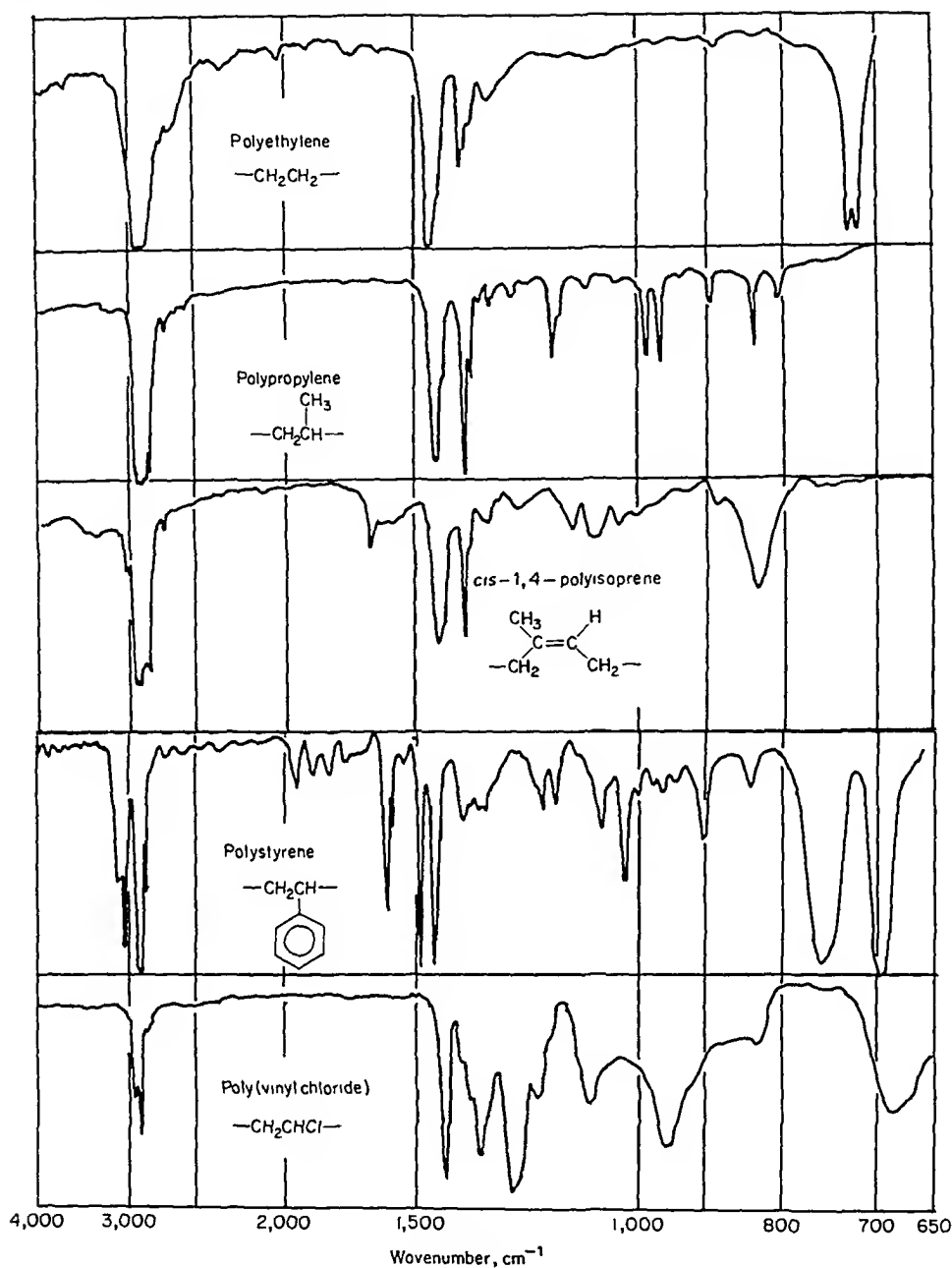
In Figs. 15-1 through 15-3 spectra for some common polymers are reproduced. Since these are transmission spectra, absorption bands appear as valleys. The characteristic band frequencies of Table 15-1 can be compared with specific polymers. The OH band appears in poly(vinyl alcohol) and not in polyethylene, for example. Spectra for the same polymer may appear differently depending on several factors. The thickness or concentration will affect the absolute value of absorption. Since the hydroxyl group in the poly(ethylene oxide) shown in Fig. 15-3 occurs as an end group, the molecular weight will affect the intensity of that band relative to the bands for the ether and hydrocarbon bonds. In poly(vinyl alcohol), Fig. 15-2, an incompletely hydrolyzed sample will show vestiges of the acetate group remaining.

Infrared analysis can be applied to surfaces [3] and to pyrolyzed fragments of polymeric materials [4] for purposes of identification.

In addition to the obvious use in identifying unknown polymers and the estimation of amounts of comonomers, impurities, or end groups in polymers, infrared analysis, with some modification, has been used for measuring crystallinity and orientation of specific groups in crystalline polymers. Chemical reactions of polymers can

TABLE 15-1
Positions of Characteristic Infrared Bands [1]

Group	Frequency range, cm^{-1}
OH stretching vibrations	
Free OH	3610–3645 (sharp)
Intramolecular hydrogen bonds	3450–3600 (sharp)
Intermolecular hydrogen bonds	3200–3550 (broad)
Chelate compounds	2500–3200 (very broad)
NH stretching vibrations	
Free NH	3300–3500
Hydrogen-bonded NH	3070–3350
CH stretching vibrations	
$\equiv\text{C}-\text{H}$	3280–3340
$=\text{C}-\text{H}$	3000–3100
$\text{C}-\text{CH}_3$	$2872 \pm 10, 2962 \pm 10$
$\text{O}-\text{CH}_3$	2815–2832
$\text{N}-\text{CH}_3$ (aromatic)	2810–2820
$\text{N}-\text{CH}_3$ (aliphatic)	2780–2805
CH_2	$2853 \pm 10, 2926 \pm 10$
CH	2880–2900
SH stretching vibrations	
Free SH	2550–2600
$\text{C}\equiv\text{N}$ stretching vibrations	
Nonconjugated	2240–2260
Conjugated	2215–2240
$\text{C}\equiv\text{C}$ stretching vibrations	
$\text{C}\equiv\text{CH}$ (terminal)	2100–2140
$\text{C}-\text{C}\equiv\text{C}$	2190–2260
$\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{CH}$	2040; 2200
$\text{C}=\text{O}$ stretching vibrations	
Nonconjugated	1700–1900
Conjugated	1590–1750
Amides	~1650
$\text{C}=\text{C}$ stretching vibrations	
Nonconjugated	1620–1680
Conjugated	1585–1625
CH bending vibrations	
CH_2	1405–1465
CH_3	1355–1395, 1430–1470
$\text{C}-\text{O}-\text{C}$ vibrations in esters	
Formates	~1175
Acetates	~1240, 1010–1040
Benzoates	~1275
$\text{C}-\text{OH}$ stretching vibrations	
Secondary cyclic alcohols	990–1060
CH out-of-plane bending vibrations in substituted ethylenic systems	
$-\text{CH}=\text{CH}_2$	905–915, 985–995
$-\text{CH}=\text{CH}-$ (cis)	650–750
$-\text{CH}=\text{CH}-$ (trans)	960–970
$\text{C}=\text{CH}_2$	885–895
	790–840

**FIGURE 15-1**

Typical transmission spectra in the infrared region [2]. The ordinate in each diagram is 0 to 100% transmission.

be followed by the appearance or disappearance of functional groups such as oxygen groups in oxidation or free hydroxyl groups from hydrolysis.

The absorption of light in the near ultraviolet (wavelengths of 0.2 to 0.4 μm , 2000 to 4000 $\text{\AA}$) arises from electronic excitation of the molecules. Two important features are that the ultraviolet absorption is generally indicative of multiple unsaturation and the absorption bands are often rather broad. One does not usually

obtain a 'fingerprint' with many individual bands as in the infrared region. On the other hand, absorption in the ultraviolet region can be quite strong and can be carried out in aqueous solutions. The column effluent from chromatographic separations of water-soluble polymers can be monitored by examining the absorption at a single wavelength.

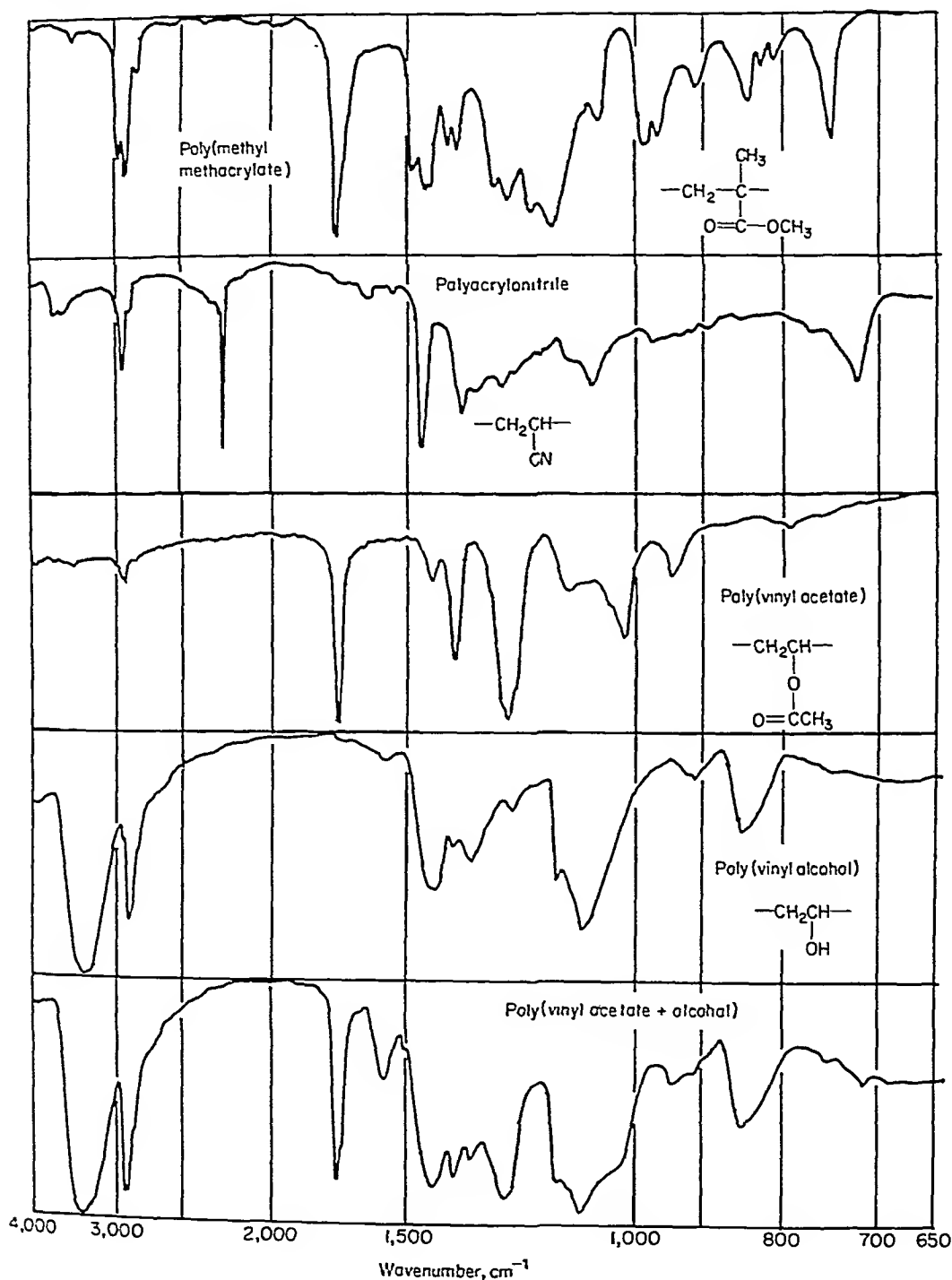
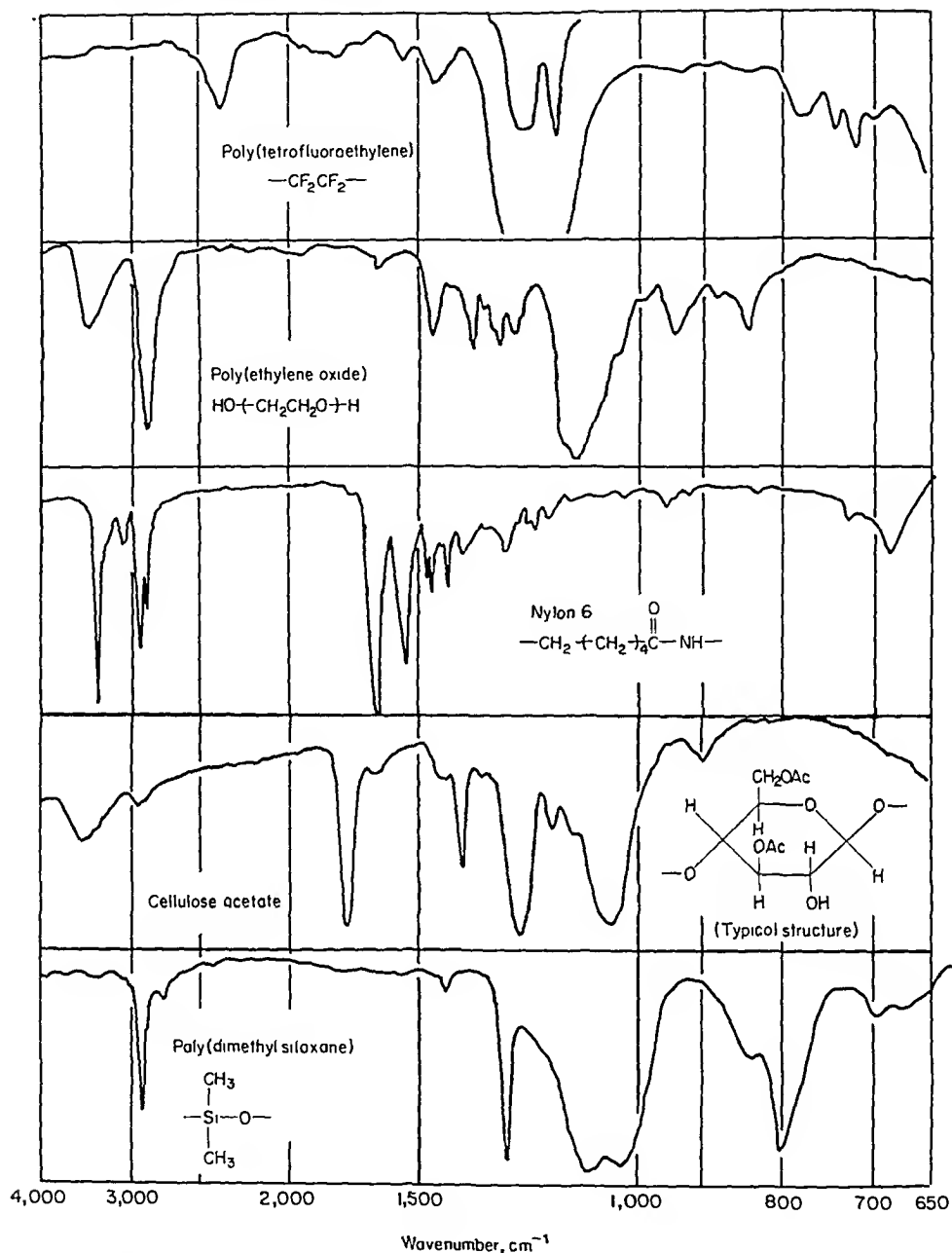


FIGURE 15-2

Typical transmission spectra in the infrared region [2]. The ordinate in each diagram is 0 to 100% transmission. The incompletely hydrolyzed sample of poly(vinyl acetate) illustrates the additivity of spectra.

**FIGURE 15-3**

Typical transmission spectra in the infrared region [2]. The ordinate in each diagram is 0 to 100% transmission. Since the cellulose acetate is made by hydrolysis of the triacetate, the structure shown is only one of many that may exist in the polymer. The average composition does correspond to the diacetate.

15-3 DIFFERENTIAL THERMAL ANALYSIS

Very often the limiting parameter for the useful application of a polymer is dimensional or chemical stability. The temperatures at which physical transitions occur are important to the first criterion, and the temperature of the onset of chemical reaction is important to the second. Some subtle changes in structure can be observed when the

polymer sample is compared to another material undergoing a similar heating process but not undergoing any transitions or reactions.

In conventional differential thermal analysis (DTA), the temperature at the center of the sample is compared with a reference material (often powdered alumina) as both are heated at a uniform rate. Any change in the sample's specific heat as at T_g , any structural change that is endothermic or exothermic as at T_m , or chemical reactions will show as changes in the temperature difference between sample T_s and reference T_r . A primitive instrument consists of thermocouples inserted in the sample and the reference. The sample and the reference material are held in a heated metal block at a controlled temperature T_0 (Fig. 15-4). As T_0 is raised (a rate of $10^\circ\text{C}/\text{min}$ is common), T_s and T_r follow perhaps by as little as 0.1°C . If an endothermic reaction takes place, T_s will lag behind T_r temporarily. If an exothermic reaction takes place, T_s will exceed T_r temporarily. A difference in specific heat between sample and reference means that $T_s - T_r$ will not be zero even when no thermal changes are occurring. However, when the specific heat of the sample changes, $T_s - T_r$ will change with a shift in the base line. These three possibilities are illustrated in Fig. 15-5. Multiple transitions in crystalline structure, recrystallization of quenched samples, stress release, reactions of impurities, and volatilization of liquids may also be detected by DTA.

Instead of measuring a finite temperature difference, *differential scanning calorimetry* (DSC) uses a servo system to supply energy at a varying rate to sample and reference so as to keep their temperatures equal. Although superficially resembling the thermogram of Fig. 15-5, a DSC output plots energy supplied vs. average temperature. By this method, the area under a peak can be directly related to the enthalpy changes occurring, whereas the area under a peak in ordinary DTA is a complex function of sample geometry, heat capacity, and heat losses.

In *thermogravimetric analysis* (TGA) a sample is weighed continuously as the temperature is raised. Volatilization, chemical reaction, and dehydration are some of the processes that affect the sample weight. When many compounds have to be screened for their applicability in a high-temperature environment, TGA may be the

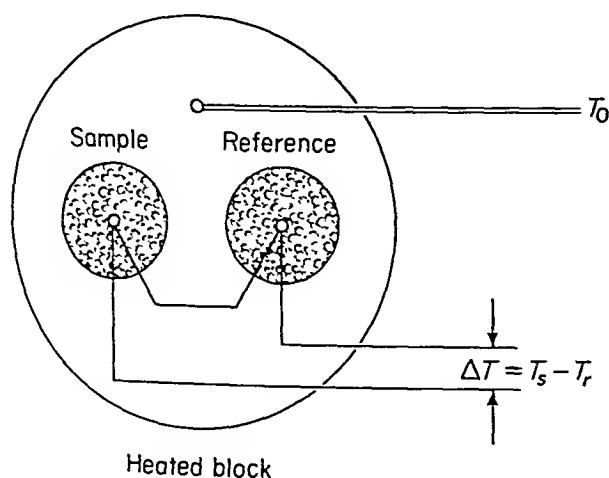


FIGURE 15-4

Schematic diagram of apparatus for differential thermal analysis (DTA). Sample and reference material are contained in a heated block that is programmed so that T_0 increases linearly with time.

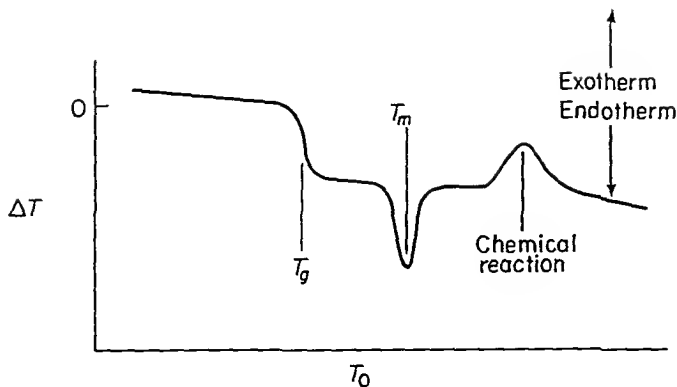


FIGURE 15-5

Scan of differential temperature vs. block temperature illustrating three possible thermal effects.

only test needed. For example, if a rubbery gasket material is needed for short-term service at 300°C, the limitation on most materials will not involve T_g or T_m . Moreover, the chemical stability may be affected by fillers, cross-linking agents, antioxidants, plasticizers, and lubricants. Whether the test is run in a vacuum or in an atmosphere of air or oxygen will be important. When TGA is combined with DTA or when the gases evolved are examined by gas chromatography, infrared spectroscopy, or mass spectroscopy, an even more complete picture of the mechanism of reaction can be put together.

Somewhat related is *torsional braid analysis* [5]. In this method the polymer is applied to a glass braid, which becomes the restoring element in a torsion pendulum. A programmed temperature rise is imposed and the dynamic mechanical properties of the system are followed. Both changes in rigidity and damping can be correlated with physical and chemical changes in the polymer structure.

15-4 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

When a compound containing hydrogen is placed in a strong magnetic field and irradiated with a radio-frequency signal, it is found that energy absorption occurs at discrete frequencies. Transitions between different spin orientation levels are taking place in the hydrogen atom. Fortunately, few of the other nuclei found in organic compounds have a net magnetic moment and spin, so that except for fluorine, chlorine, and certain isotopes of carbon, nitrogen, and oxygen, the only effects seen are those of the protons. It is fortunate, also, that the exact frequency at which energy is absorbed is very sensitive to the atomic environment of the proton. The scan of absorption vs. frequency for ethanol, for example, gives three widely separated peaks with areas in the ratio 1:2:3. Tetramethyl silane, in which all the protons are equivalent, is often used as an internal standard and assigned a frequency value τ of 10. Most other protons have values of τ between 0 and 10, representing various degrees of *chemical shift* of the fundamental frequency by environment.

In practice about 0.5 ml of polymer solution (say, 10% in an aprotic solvent such as carbon tetrachloride) is placed in a thin-glass tube between the poles of a

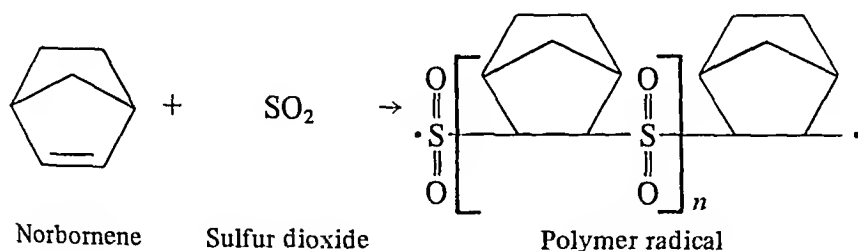
strong magnet having a field strength of about 10,000 gauss. A radio-frequency field is imposed on the sample at right angles to the magnetic field. Various devices are used to detect the absorption of energy at resonance as the protons undergo changes in spin orientation level.

Some typical spectra (Fig. 15-6) show the broadening of the peaks in the polymer compared with small molecules because of the lower mobility in the polymer. Of course, the hydroxyl peak at $\tau = 4.2$ appears only in the alcohol in this series. The chain CH peak in the polymer underlies the CH_2 multiplet at $\tau = 6.3$ to 6.6 and is not seen separately.

The applications of NMR spectroscopy, in addition to compositional analysis, include the detection of isotactic-atactic ratios, monomer sequence distributions in copolymers, and other configurational variations. A narrowing of the resonance peak is typical at phase transitions, making it possible to use NMR of solid polymers to measure T_g and T_m .

A related technique using microwave frequencies is capable of detecting the changes in energy levels due to the magnetic moment of electrons. Such *electron paramagnetic resonance* (EPR), also called *electron spin resonance* (ESR), can be studied when there is a net unpaired electronic magnetic moment in the molecule being investigated. Free radicals from polymerization or oxidation, especially long-lived ones trapped in the glassy solid state, can be measured. In most free-radical polymerizations, the radical concentration is down around 10^{-8} mol/liter and is difficult to detect by EPR. The bulk copolymerization of norbornene and sulfur dioxide, however, appears to proceed with radical concentrations of around 10^{-5} mol/liter, so that detection of radicals at room temperature over a period of hours and weeks is feasible [7].

The structure of these "living" polymers is postulated as



15-5 MISCELLANEOUS SPECTROSCOPIC METHODS

Many new methods of analysis have been extended to polymer systems. Some newer techniques include [8, 9, 10]:

1. Fourier transform infrared analysis by which the entire spectrum can be scanned in about 20 s.
2. Raman spectroscopy for analysis of chain-stretching motions in lamellar regions.
3. Carbon-13 NMR using computer-enhancement of weak signals; "magic-angle" (54.7°) spinning with cross-polarization to reduce broadening of lines [11].
4. Neutron scattering which extends dynamic light scattering techniques to movements of very small chain segments.

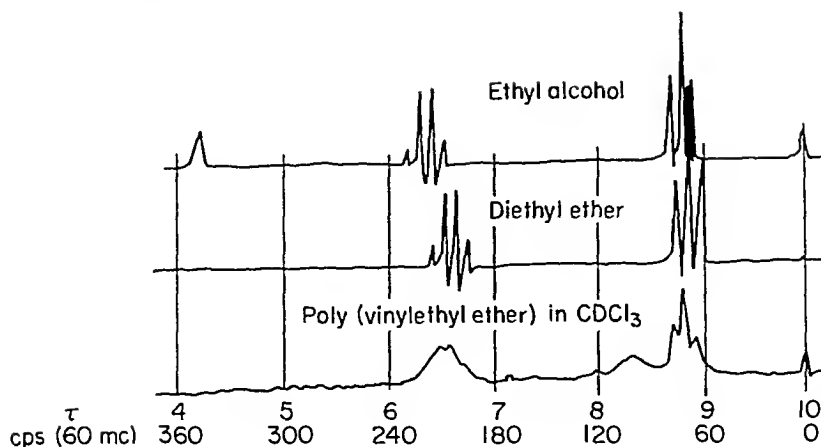


FIGURE 15-6

A comparison of the proton magnetic resonance spectra of ethanol, diethyl ether, and poly(vinyl ethyl ether) [6].

5. Analysis of electrons ejected when a polymer surface is bombarded with x-rays (ESCA, electron spectroscopy for chemical analysis). The energy spectrum can be used to identify the chemical species present in the surface layers.

15-6 CHEMICAL TESTS AND IDENTIFICATION SCHEMES

There are many ways by which polymers may be identified. In textile fibers, microscopic examination of the cross section and texture may be sufficient for the more complex, naturally occurring polymers. Solubility for the more complex, naturally occurring polymers. Solubility and staining tests can also be used. These have been summarized by Morrison [12]. When a polymer or compound ingredient can be extracted and made into a film or pressed wafer, the infrared spectrum may be the most direct and most powerful tool available. An analytical scheme for identifying many common plastics is given by Gruben and Leiner [13]. Other "spot" tests have been suggested by Feigl [14, 15]. As a general rule it is best to try to separate a sample suspected of being a mixture by extraction before attempting to carry out chemical tests. Plasticizers, antioxidants, surfactants, and other small molecules are usually not bound chemically to the polymer and should be removed by preliminary treatment. Thin layer chromatography (TLC) has been used mainly for identification of compounding ingredients that have been extracted from a product, but it can be used for low-molecular-weight polymers also [16, 17].

PROBLEMS

15-1. Three samples of flexible tubing are subjected to the following tests:

- (a) Held in burner flame. Tubes A and C burn.
- (b) Soaked overnight in chloroform. Tube A swells, B becomes very stiff and somewhat smaller on drying out, C is unaffected.
- (c) Immersed in a lead nitrate solution. A turns black; B and C are unaffected.

Which of the three is vulcanized rubber, polyethylene, or plasticized poly(vinyl chloride)?

- 15-2. Try to identify the group associated with the four most prominent absorption bands in poly(vinyl acetate). Use Table 15-1 as a guide.
- 15-3. One characteristic property by which unmodified polystyrene can often be identified is the clattering sound made by dropping a molded piece on a hard surface. An inexpensive protractor or comb tossed on a table top can be identified this way. What factors might be involved in causing this property?
- 15-4. How would microscopic observation of the cross section of a fiber sample differentiate between nylon 6 and rayon?
- 15-5. A sample of rubber shows no flow in a creep experiment, indicating that it is cross-linked. It contains no fillers. What additional simple tests might be run to decide whether the material is natural rubber, styrene-butadiene rubber, or acrylonitrile-butadiene rubber?
- 15-6. You are given a material to identify. It is in the form of a stiff, transparent sheet about 0.01 in thick. It burns slowly with a smell of vinegar. It dissolves completely in acetone. Is it polyethylene, polypropylene, poly(vinyl chloride), poly(vinyl acetate), nylon 6, or cellulose diacetate?

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APPENDIX

7

LIST OF SYMBOLS

Symbol	Common unit	Definition or label	Section where first used
A	Variable	Used as an arbitrary constant	
A	cm^2, in^2	Area	7-1
A_t	m^2	Total surface area of particles	5-5
A_u	cm^2	Area, original unstretched	8-2
A, A_p, A_i, A_t	s^{-1}	Collision frequency factors	4-4
A_2	$\text{dl} \cdot \text{mol/g}^2$	Second virial coefficient	6-6
A_3	$\text{dl}^2 \cdot \text{mol/g}^3$	Third virial coefficient	6-6
$\text{\AA}$		Angstrom unit, 10^{-10} m	
B	Variable	Used as an arbitrary constant	
C_2	Pa	Constant in Eq. (8-24)	8-2
C_f	farad	Capacitance	10-6
C_i, C_s	...	Chain transfer constant	5-5
C_z	Variable	Lumped constant	7-7
C'	$(\text{mol/g})^{1/2}$	Constant in Eq. (7-11)	7-3
CED	cal/cm^3	Cohesive energy density	2-5
D	...	Abbreviation for bifunctional unit	14-7
$D, D_i, \bar{D}_L, \bar{D}_A, \bar{D}_V$	cm, in	Diameter or average diameter	6-1
D_b	cm	Barrel diameter inside extruder	12-5
D_s	cm	Diameter of extruder die	7-8
ΔE_v	cal	Internal energy of vaporization	2-5
E	Pa	Young's modulus	8-1
$E(\theta)$	Pa	Distribution of relaxation times	8-4

Symbol	Common unit	Definition or label	Section where first used
$E(t)$	Pa	Time-dependent modulus	8-3
E_i	Pa	Modulus of individual element	8-5
E_r	Pa	Modulus measured in stress-relaxation mode	11-3
E_t	Pa	Modulus measured intermittently	11-3
E_T	Pa	Modulus of an array of elements	8-5
E^*	Pa	Complex modulus	8-3
E'	Pa	Real part of complex modulus	8-3
E''	Pa	Imaginary part of complex modulus	8-3
ϵ	V	Voltage	10-6
F_1, F_2	...	Mole fractions of monomers 1 and 2 in polymer	4-7
ΔF_m	cal	Free energy of mixing	2-5
G	Pa	shear modulus	8-1
G_s	Pa	Shear modulus in Pao-Rouse model	7-8
$\dot{g}$	J/m ²	Strain energy release rate	9-7
ΔH_f	cal/mol	Enthalpy of fusion, pure solvent	6-6
H_p	hp	Horsepower	12-5
ΔH_p	J/mol	Enthalpy of polymerization	5-1
ΔH_u	J/mol	Enthalpy of fusion for polymer repeat unit	3-4
ΔH_v	J/mol	Enthalpy of vaporization	2-5
H'	Variable	Lumped constant in Debye equation	6-8
$\bar{H}(\log \theta)$	Pa·s	Distribution of relaxation times	8-4
$[I]$	mol/liter	Initiator concentration	4-4
I_g	lumen	Light scattered	6-7
I_{gs}	lumen	Light scattered by solvent	6-7
I_m, I_r	g·cm ²	Moment of inertia	8-3
J	Pa ⁻¹	Compliance	8-1
K, K', K''	Variable	Constants in Eqs. (7-16), (7-22), and (7-31)	7-3
K_{Ic}	MPa·m ^{1/2}	Critical stress intensity factor or fracture toughness	9-7
K_0	s ⁻¹	Constant rate of strain	8-3
K_c	...	Dielectric constant	10-6
L	cm	Length	7-7, 8-1

Symbol	Common unit	Definition or label	Section where first used
L_u	cm	Unstressed length	8-1
M	g	Mass	7-1
M	...	Used as an abbreviation for monofunctional unit	14-7
M	g/mol	Molecular weight	6-1
$[M]$	mol/liter	Monomer concentration	4-4
$[M\cdot]$	mol/liter	Concentration of radical chains	4-4
M_n	g/mol	Number average molecular weight	6-1
M_v	g/mol	Viscosity average molecular weight	7-3
M_w	g/mol	Weight average molecular weight	6-1
M_0	g/mol	Molecular weight of repeat unit	6-2
M_i, M_1, M_2	g/mol	Molecular weight of specific components	6-1, 6-6
N	...	Number of items	7-6, 9-2
N, N_i, N_1, N_2	mol	Number of moles of specific components	4-5, 4-7, 6-3, 11-3
N_E, N_A, N_D			
N_o, N_c, N_s			
N	mol/cm ³	Moles of polymer chains per unit volume	8-2
N	mol/liter	Concentration of monomer units per unit volume	11-3
N_p	mol/liter	Concentration of particles per unit volume	5-5
$P, P(0, N_2),$ etc.	dyn/cm ² , Pa	Pressure	6-6
$P(\theta)$	...	Complex function of rotation angle	6-8
P_n	Pa	Normal stress coefficient	7-8
$(P_r)_x$	...	Probability or mole fraction of x-mer	6-2
$\Delta P/L$	Pa/m	Pressure drop per unit length	7-7
Q	...	Used as an abbreviation for tetrafunctional monomer unit	14-7
Q	...	Constant in Price-Alfrey scheme	4-7
Q	cm ³ /s	Volumetric rate of flow	7-6
Q_e	kg/h	Extruder capacity	12-5
$\dot{Q}$	J/s	Rate of energy dissipation in viscous flow	7-2
R	cal/mol·deg	Gas constant	4-4
R_p	mol/liter·s	Rate of polymerization	

Symbol	Common unit	Definition or label	Section where first used
$[R\cdot]$	mol/liter	Concentration of initiator radicals	4-4
$[R_s]$	mol/liter	Concentration of initiator seeds	4-6
S	J/K	Entropy	8-2
$[S]$	mol/liter	Surfactant concentration	5-5
T	...	Used as an abbreviation for a trifunctional monomer unit	14-7
T	K	Temperature	
T_f	K	Freezing temperature of pure solvent	6-6
T_g	K	Glass-transition temperature	3-5
T_m	K	Melting temperature	3-4
$(T_m)_0$	K	Melting temperature, pure polymer	3-4
T_R	K	Reference temperature	7-5
τ	N·m	Torque	7-7
U_p	W	Power used in dielectric heating	10-6
V	cm ³	Volume	8-1
$\bar{V}$	cm ³ /g	Specific volume	7-5
V_f	cm ³ /g	Free volume	7-5
V_g	cm ³ /mol	Molar volume of solvent as vapor	2-5
V_0	cm ³ /g	Specific volume extrapolated to 0 K	7-5
V_r	cm ³	Effluent volume	6-4
$V_r(M)$	cm ³	Effluent volume for molecular weight M	6-4
V_u	cm ³	Original volume	3-4
V_1	cm ³ /mol	Molar volume of solvent	2-5
W	J	Work	8-2
W_i	g	Weight of component i	6-1
W_x	g	Weight of x -mer	6-2
X	...	The ratio of f_1/f_2	4-7
Y	...	The ratio of F_1/F_2	4-7
Z_w	...	Weight average number of chain atoms, $M_w/(\text{mol wt per chain atom})$	7-4
a	...	Constant in Eqs. (7-16), (7-30)	7-3, 7-5
a	cm	Bond length	7-2
a	...	$x_n/(x_w - x_n)$	6-3
a	cm	Thickness	8-1

Symbol	Common unit	Definition or label	Section where first used
a	m^2	Surface area of a particle	5-5
a_s	m^2	Area occupied by a mole of surfactant	5-5
a_T	...	Shift factor	8-3
b	cm	Width	8-1
c	gm/dl, gm/cm^3	Concentration	6-6
c	cm/s	Velocity of light in vacuum, 3.00×10^8 cm/s	11-1
c_p	$\text{cal}/\text{g}\cdot^\circ\text{C}$	Specific heat	12-5
c_r	cm	Crack length	9-8
d	cm	Plate spacing, sample thickness	10-6
e	...	Polarity parameter in Price-Alfrey scheme	4-7
f	...	Frequency factor	4-4
f	...	Functionality of monomer	4-2, 4-5
f	newtons	Force	7-1
f_1, f_2	...	Mole fraction in monomer feed	4-7
f', f'_g	...	Fractional free volume at temperature T or T_g	7-5
h	cm	Height	6-6
i	...	Subscript referring to component i	
i	...	Denoting imaginary part of complex variable, square root of -1	
k	Variable	Arbitrary factor in non-Newtonian equations	7-6
$k, k_i, k_t, k_p,$ $k_2, k_3, k_4,$ $k_{12}, k_{22}, k_{21},$ k_{11}	Variable Variable	Rate constants	4-4, 4-7
k_c k', k'', k''', k_L	$\text{W}/\text{m}\cdot^\circ\text{C}$ Variable	Thermal conductivity Constants in equations for concentration dependence of viscosity	10-6
m	mol/liter	Concentration of polymer molecules	7-3
m	g	Masses used in torsion pendulum	11-3
n	...	Exponent in power law	8-3
n	...	Sample index number	-7-6
R_3, R_4	ohm	Electrical resistance	9-2 10-6

Symbol	Common unit	Definition or label	Section where first used
n	...	Number of links in freely oriented chain	7-2
p	Pa	Vapor pressure	2-5
p	...	Fraction of monomer converted to polymer	6-2
p	...	Summing index in Rouse model	7-6
P_B, P_F	...	Fraction of monomer converted to polymer at gelling point for bifunctional B monomer and polyfunctional F monomer	4-5
r	cm	Radius	7-7
r	...	Ratio of hydroxyl to carboxyl groups	4-5
r_1, r_2	...	Relative reactivity ratios	4-7
$(\bar{r}^2)^{1/2}$	cm	Root-mean-square end-to-end distance	7-2
$(\bar{r}_0^2)^{1/2}$	cm	Root-mean-square end-to-end distance in a theta solvent	7-2
s	...	Standard deviation	9-2
$(\bar{s}^2)^{1/2}$	cm	Radius of gyration	7-2
t	s	Time	
u	cm/s	Velocity	7-2
u_e	J	Energy loss per cycle	8-3
v	m ³	Particle volume	5-5
v_1, v_2	...	Volume fractions of components 1 and 2	2-5, 3-4
w_i	...	Weight fraction of component i	3-5
w_x	...	Weight fraction of x -mer	6-2
x	...	Degree of polymerization (also x_w, x_n , etc.)	4-4
x	...	Mole fraction of one component in liquid phase	4-7
y	cm	Distance	7-1
z	...	Exponent in power law	7-6
z	...	$d(\ln \bar{\gamma})/d(\ln \tau)$	7-6
$\Gamma(a+1)$	...	Gamma function of $a+1$	6-3
Δ	...	Signifies difference	
Δ	...	Logarithmic decrement	8-3
Λ	Pa	Factor in Eq. (8-25)	8-3
Σ	...	Summation sign	
Υ	...	Coupling-Disproportionation factor	4-4

Symbol	Common unit	Definition or label	Section where first used
Φ	...	Constant in Eq. (7-20), $2.1 \pm 0.2 \times 10^{21}$ dl/g·mol·cm ³	7-3
$\Omega, \Omega_b, \Omega_c$	rad/s	Rate of rotation, also referred to bob or cup	7-3, 7-7
Ω_1, Ω_2	...	Probabilities of states 1 and 2	8-2
α	...	In Eq. (4-38), $\alpha = r_2/(1 - r_2)$	4-7
α	...	Expansion factor, $(r^2/r_0^2)^{1/2}$	7-2
α	K ⁻¹	Volumetric coefficient of thermal expansion for melt minus that of glass	7-5
$\alpha, \alpha_x, \alpha_y, \alpha_z$	...	Extension ratio, also in x, y , and z directions	8-1, 8-2
α_e	K ⁻¹	Linear coefficient of thermal expansion	10-5
α_r	...	Relative volatility	4-7
β	...	In Eq. (4-38), $\beta = r_1/(1 - r_1)$	4-7
β	g/mol	Constant in Eq. (7-30)	7-5
β	...	Die swell	7-8
β	...	Normalizing factor	8-2
γ	...	Shear strain	7-1, 8-1
γ	...	A constant, function of r_1 and r_2 in Eq. (4-38)	4-7
γ_c	dynes/cm	Critical surface tension	12-4
γ_e	mN/m, J/m ²	Specific surface energy	9-7
$\dot{\gamma}$	s ⁻¹	Rate of shear, $d\gamma/dt$	7-1
$\dot{\gamma}_w$	s ⁻¹	Rate of shear at wall	7-6
$(\dot{\gamma}_w)_a$	s ⁻¹	Apparent rate of shear at wall	7-6
$\dot{\gamma}_{gm}$	s ⁻¹	Rate of shear at geometric-mean-radius	7-7
$\dot{\gamma}^+$	s ⁻¹	Rate of shear at reference radius	7-7
δ	...	A constant, function of r_1 and r_2 in Eq. (4-38)	4-7
δ	...	Loss angle	8-3
$\delta, \delta_1, \delta_2$	(cal/cm ³) ^{1/2} (Hildebrand)	Solubility parameter, also referred to components 1, solvent, and 2, polymer	2-5
$\sin \delta$	...	Power factor	10-6
$\tan \delta$	...	Dissipation factor	8-3, 10-6
ϵ	...	Elongation, $\epsilon = \gamma - 1$	8-1
ϵ_b	...	Elongation at break	9-6
ϵ_1, ϵ_2	...	Elongation of components 1 and 2 in Maxwell model	8-3

Symbol	Common unit	Definition or label	Section where first used
$\dot{\epsilon}$	s^{-1}	Rate of elongation, $d\epsilon/dt$	8-3
$\dot{\epsilon}_{ij}$	s^{-1}	Rate of strain tensor	7-8
η	$Pa \cdot s$	Viscosity	7-1
η_0, η_∞	$Pa \cdot s$	Viscosity at low and high shear rates	7-6
η_g, η_R	$Pa \cdot s$	Viscosity at T_g and at T_R	7-5
η_{sp}	...	Specific viscosity, $\eta_r - 1$	7-3
η_{sp}/c	dl/g	Reduced viscosity	7-3
η_r	...	Relative viscosity, η/η_s	7-3
η_s	...	Solvent viscosity	7-3
$[\eta]$	dl/g	Intrinsic viscosity	7-3
$[\eta]_\theta$	dl/g	Intrinsic viscosity at theta temperature	7-3
η'	$Pa \cdot s$	Dynamic viscosity	8-3
$(\ln \eta_r)/c$	dl/g	Inherent viscosity	7-3
θ	degree	Supplement of bond angle	7-2
θ	s	Relaxation time	8-2
θ_c	degree	Contact angle	12-4
θ_f	K	Flory temperature (theta temperature)	7-2
θ'	degree	Bond angle	7-2
λ	m	Wavelength	11-1
λ	...	Coefficient in Eq. (8-25)	8-3
μ	m^3/s	Particle growth rate	5-5
μ	...	Geometric factor in Eq. (8-4)	8-1
μ_i	Pa	Modulus in Pao equation (7-45)	7-6
ν	...	Poisson's ratio	8-1
ν_n	Variable	Kinetic chain length	4-4
π	Pa	Osmotic pressure	6-6
π		3.14159 ...	
ρ	g/cm^3	Density	6-6
ρ_i	...	Ratio of reactive groups on reactant i to all groups that react the same way in the system	4-5
ρ_r	ohm $\cdot$ cm	Volume resistivity	10-6
ρ_r	radicals/s	Rate of radical generation	5-5
σ	Pa	Tensile stress	8-1
σ	...	Steric factor	7-2
σ_b	Pa	Stress at break	9-1
$\sigma_b(n)$	Pa	Stress at break for n th sample	9-1

Symbol	Common unit	Definition or label	Section where first used
$\overline{\sigma_b}$	Pa	Modal strength for sample population	9-1
σ_i	Pa	Stress in element i	8-4
σ_0	Pa	Fixed stress	8-3
σ_T	Pa	Total stress of an array of elements	8-4
τ	Pa	Shear stress	7-1
τ	s	Time of particle formation	5-5
τ_{gm}	Pa	Shear stress at geometric-mean-radius	7-7
τ_w	Pa	Shear stress at wall	7-7
τ_{ij}	Pa	Stress tensor	7-8
ϕ	degree	Bond rotation angle	7-2
ϕ_i	s	Relaxation time	7-6
ϕ_0	s	Maximum relaxation time	7-6, 7-8
$[\phi]$	mol/liter	Concentration of ester bonds	11-3
χ	...	Polymer-solvent interaction parameter	2-5
ψ	degree	Cone angle	7-7
ψ'	degree	Angle of twist	8-1
ω	rad/s	Frequency	7-3
ω_c	Hz (cycle/s)	Frequency	10-6

APPENDIX

2

HARMONIC MOTION OF A MAXWELL MODEL

A2-1 TRIGONOMETRIC NOTATION

Starting with a sinusoidal input of strain in a Maxwell element (Sec. 8-3), we derive the resulting sinusoidal stress. First we let the strain ϵ be a function of a maximum strain ϵ_m and time t with a frequency ω .

$$\epsilon = \epsilon_m \sin \omega t \quad (\text{A2-1})$$

For the Maxwell element:

$$\frac{d\epsilon}{dt} = \frac{1}{E} \frac{d\sigma}{dt} + \frac{\sigma}{E\theta} \quad (\text{A2-2})$$

Differentiating Eq. (A2-1):

$$\frac{d\epsilon}{dt} = \epsilon_m \cos \omega t \quad (\text{A2-3})$$

Rearranging Eq. (A2-2):

$$\frac{d\sigma}{dt} + \frac{\sigma}{\theta} = \omega \epsilon_m E \cos \omega t \quad (\text{A2-4})$$

This is a simple linear differential equation of the form

$$\frac{dy}{dx} + Py = Q$$

The general solution for such an equation, when P and Q are functions of x only, is

$$y \exp(\psi) = \int \exp(\psi) Q dx + C \quad \psi = \int P dx \quad (\text{A2-5})$$

For Eq. (A2-4), the analogy is

$$\psi = \frac{t}{\theta} \quad (\text{A2-6})$$

$$\sigma \exp\left(\frac{t}{\theta}\right) = \omega \epsilon_m E \int \exp\left(\frac{t}{\theta}\right) \cos \omega t dt + C \quad (\text{A2-7})$$

$$\sigma \exp\left(\frac{t}{\theta}\right) = \frac{\omega \epsilon_m E \theta}{1 + \omega^2 \theta^2} (\cos \omega t + \omega \theta \sin \omega t) \exp\left(\frac{t}{\theta}\right) + C \quad (\text{A2-8})$$

$$\text{or } \sigma = \frac{\omega \theta}{1 + \omega^2 \theta^2} \epsilon_m E (\cos \omega t + \omega \theta \sin \omega t) + C \exp\left(\frac{-t}{\theta}\right) \quad (\text{A2-9})$$

The second term on the right is a transient one that drops out in the desired steady-state solution for $t/\theta \gg 1$.

We define an angle δ by

$$\tan \delta = \frac{1}{\omega \theta} = \frac{\sin \delta}{\cos \delta} \quad \text{and} \quad \sin \delta = \frac{1}{(1 + \omega^2 \theta^2)^{1/2}} \quad (\text{A2-10})$$

Then, making use of trigonometric identities:

$$\cos \omega t + \omega \theta \sin \omega t = \frac{\cos \omega t (\sin \delta)}{\sin \delta} + \frac{\sin \omega t (\cos \delta)}{\sin \delta} \quad (\text{A2-11})$$

$$= \frac{\sin(\omega t + \delta)}{\sin \delta} \quad (\text{A2-12})$$

$$= (1 + \omega^2 \theta^2)^{1/2} \sin(\omega t + \delta) \quad (\text{A2-13})$$

Finally, combining Eqs. (A2-13) and (A2-9) with the transient term dropped, we arrive at

$$\sigma = \frac{\omega \theta}{(1 + \omega^2 \theta^2)^{1/2}} \epsilon_m E \sin(\omega t + \delta) \quad (\text{A2-14})$$

A2-2 COMPLEX NOTATION

In this case, we start with a complex strain, the real part of which is the actual strain:

$$\epsilon^* = \epsilon_m \exp(i\omega t) \quad (\text{A2-15})$$

The motion of the Maxwell element, in terms of a complex stress and strain, is

$$\frac{d\sigma^*}{dt} = \frac{1}{E} \frac{d\sigma^*}{dt} + \frac{\sigma^*}{E\theta} \quad (\text{A2-16})$$

Differentiating Eq. (A2-15):

$$\frac{d\epsilon^*}{dt} = i\omega a_m \exp(i\omega t) \quad (\text{A2-17})$$

Rearranging Eqs. (A2-16) and (A2-17):

$$\frac{d\sigma^*}{dt} + \frac{\sigma^*}{\theta} = E \frac{d\epsilon^*}{dt} = i\omega \epsilon_m E \exp(i\omega t) = Q \quad (\text{A2-18})$$

As in App. A2-1, the general solution is

$$\sigma^* \exp\left(\frac{t}{\theta}\right) = \int \exp\left(\frac{t}{\theta}\right) Q dt + C \quad (\text{A2-19})$$

$$\int \exp\left(\frac{t}{\theta}\right) Q dt = i\omega \epsilon_m E \int \exp\left(i\omega t + \frac{t}{\theta}\right) dt = \frac{i\omega \epsilon_m E \exp(i\omega t + t/\theta)}{i\omega + 1/\theta} \quad (\text{A2-20})$$

Substitution and rearrangement with Eq. (A2-19) yields

$$\sigma^* = \frac{i\omega \epsilon_m \theta E \exp(i\omega t)}{i\omega \theta + 1} + C \exp\left(-\frac{t}{\theta}\right) \quad (\text{A2-21})$$

Once again, the second term on the right-hand side is a transient term which drops out at $t/\theta \gg 1$. Multiplying both numerator and denominator by $1 - i\omega\theta$ and substituting ϵ^* for its equivalent $\epsilon_m \exp(i\omega t)$ gives

$$\sigma^* = \frac{\omega^2 \theta^2 \epsilon^* E + i\omega \theta \epsilon^* E}{1 + \omega^2 \theta^2} \quad (\text{A2-22})$$

The definition of complex modulus E^* is

$$E^* = E' + iE'' = \frac{\sigma^*}{\epsilon^*} \quad (\text{A2-23})$$

But Eq. (A2-22) gives

$$\frac{\sigma^*}{\epsilon^*} = \frac{E\omega^2 \theta^2}{1 + \omega^2 \theta^2} + \frac{i(E\omega \theta)}{1 + \omega^2 \theta^2} \quad (\text{A2-24})$$

Identifying Eqs. (A2-23) and (A2-24) together, we conclude that

$$E' = \frac{E\omega^2\theta^2}{1 + \omega^2\theta^2} \quad \text{and} \quad E'' = \frac{E\omega\theta}{1 + \omega^2\theta^2} \quad (\text{A2-25})$$

By the conventions of complex notation we find a loss angle δ , where

$$E^* = [(E')^2 + (E'')^2]^{1/2} \exp(i\delta) \quad \text{and} \quad \tan \delta = \frac{E''}{E'} \quad (\text{A2-26})$$

From Eqs. (A2-25):

$$\tan \delta = \frac{1}{\omega\theta} \quad (\text{A2-27})$$

$$[(E')^2 + (E'')^2]^{1/2} = \frac{E\omega\theta}{(1 + \omega^2\theta^2)^{1/2}} \quad (\text{A2-28})$$

Also

$$\sigma^* = E^* \epsilon^* = \frac{E\omega\theta\epsilon^*}{(1 + \omega^2\theta^2)^{1/2}} \exp(i\delta) \quad (\text{A2-29})$$

The actual stress σ is the real part of σ^* . Equation (A2-29) shows that σ^* depends on E and ϵ^* but leads by an angle δ . The maximum value of stress σ_m occurs at $\omega t + \delta = 0$.

$$\sigma_m = \frac{E\omega\theta\epsilon_m}{(1 + \omega^2\theta^2)^{1/2}} \quad \text{and} \quad \sigma^* = \sigma_m \exp(i\omega t + i\delta) \quad (\text{A2-30})$$

Also we can write

$$E' = \frac{\sigma_m \omega \theta}{\epsilon_m (1 + \omega^2 \theta^2)^{1/2}} \quad (\text{A2-31})$$

Thus we can evaluate E , θ , E' , or E'' from experimental measurement of ϵ_m , σ_m , and δ at a known value of ω .

APPENDIX

3

A GUIDE TO LITERATURE SOURCES

Before 1946 publications in polymer science were scattered throughout the literature in journals that included work in many branches of chemistry and physics. With the advent of the *Journal of Polymer Science*, *Die Makromolecular Chemie*, and others, most polymer work now appears in specialized journals. The listings below contain journal title together with publisher and in most cases location of publication if not in United States, and number of issues per year. Publishers' addresses can be located in *Chemical Abstracts* or in "Ulrich's International Periodicals Directory, 1979-1980," R. R. Bowker Co., New York, 1979, or in "The Standard Periodical Directory," 6th ed., 1979-80, Oxbridge Communications, Inc., New York, 1978. The large number of publications has made more important the organization of reviews and abstract services that are mentioned in separate categories below. Such sources as trade associations and government bureaus are listed along with extensive literature sources in the monographs by E. R. Yescombe, "Plastics and Rubbers: World Sources of Information," Applied Science Publishers, Barking, Essex, England, 1976, and in an earlier volume, "Sources of Information of the Rubber, Plastics, and Allied Industries," Pergamon, New York, 1968.

The listings below are not complete. However, most English-language journals are listed, especially those available in the United States. The letters F.L. before a title indicate that some papers are in a language other than English. English summaries are almost always printed. The most common second language in these journals is German, although Russian, French, and Italian occur also.

A3-1 REVIEWS AND SUMMARIES

- A. Annual "encyclopedia" or "yearbook" issues. Most of these list tradenames and sources of supply. Some contain summaries of typical properties and production figures as well.

1. *Hydrocarbon Processing*, Gulf. A review of many monomer and polymer production processes is included in the Petrochemical Handbook Issue each November in odd-numbered years.
 2. *Insulation*, Lake. *Insulation Directory/Encyclopedia* in the June/July issue.
 3. *Materials Engineering*, Reinhold. *Materials Selector Issue*, second part of October each year.
 4. *Modern Plastics*, McGraw-Hill. *Modern Plastics Encyclopedia*, second issue in October each year.
 5. *Rubber Red Book*, Palmerton. An annual directory of the rubber industry.
 6. *Textile World*, McGraw-Hill. *Man-Made Fiber Chart*, included in the August issue in even-numbered years.
- B. Annual or periodic reviews. Usually the title of the review or journal suggests the main emphasis to be found in the article. However, some, such as the technology review in *Modern Plastics*, have grown to include much fundamental work in polymerization and characterization. An annotated guide to review articles in journals has been assembled by M. S. M. Alger in "Index of Reviews in Polymer Science," RAPRA, Shrewsbury, England, 1977. Textbooks and monographs are not included.
1. *Chemical and Engineering News*, ACS. An annual review of chemical industry production figures appears each September.
 2. *Modern Plastics*, McGraw-Hill. An annual review of plastics production data is included in the January issue.
 3. *Modern Plastics*, McGraw-Hill. An annual review of plastics technology is featured in the February issue. Usually over a thousand references.
 4. *Reports on the Progress of Applied Chemistry* (Annual), Society of Chemical Industry, London. Section on Plastics, Synthetic Fibres, and Resins.
 5. *Review of Textile Progress* (Annual), The Textile Institute and the Society of Dyers and Colourists, Butterworths.
 6. *Statistical Abstract of the United States*, U.S. Dept. of Commerce. Special tables on chemicals, plastics, elastomers, and fibers.
- C. Reviews of specific topics. These differ from the preceding two categories in that the same subject is not usually repeated periodically. Even in hard-cover editions, there may be no overall emphasis, so that the individual topics within one volume may bear no relation to one another. They differ from collections of papers from meetings or symposia in that they are reviews and seldom introduce original work.
1. *Advances in Macromolecular Chemistry*, Academic Press (vol. I, 1968).
 2. *Encyclopedia of Polymer Science and Technology*, Wiley (vols. 1-16, 1964-1972)
 3. (F.L.) *Fortschritte der Hochpolymeren Forschung*, or *Advances in Polymer Science*, Springer-Verlag, 4/year.
 4. *Journal of Macromolecular Science, Part C, Reviews*, Dekker, 2/year.
 5. *Journal of Macromolecular Science, Part D, Reviews in Polymer Processing and Technology*, Dekker, 2/year.
 6. *Macromolecular Reviews*, Wiley, irreg.
 7. *Progress in High Polymers*, Heywood (vol. I, 1961; vol. II, 1964).
 8. *Progress in Polymer Science*, Pergamon (vol. I, 1967).

9. *Rubber Chemistry and Technology*, Division of Rubber Chemistry, ACS. Usually one of the five issues is devoted to reviews of such subjects as polymer structure, rubber reinforcement, cross-linking, and others.

A3-2 JOURNALS DEVOTED TO RESEARCH AND DEVELOPMENT IN POLYMER SCIENCE

A. Journals primarily oriented toward polymers.

1. (F.L.) *Die Angewandte Makromolekulare Chemie*, Hüthig and Wepf Verlag, Basel, 5/yr.
2. *Biopolymers*, Wiley, 12/year.
3. (F.L.) *Colloid and Polymer Science*, Dr. D. Steinkopff Verlag, 12/year.
4. (F.L.) *European Polymer Journal*, Pergamon, London, 12/year.
5. *International Journal of Polymeric Materials*, Gordon and Breach, 4/year.
6. *Journal of Applied Polymer Science*, Wiley, 12/year.
7. *Journal of Elastoplastics* (Elastoplastics Division of SPI), Technomic, 4/year.
8. *Journal of Macromolecular Science, Part A, Chemistry*, Dekker, 8/year.
9. *Journal of Macromolecular Science, Part B, Physics*, Dekker, 4/year.
10. *Journal of Polymer Science, Part A-1, Polymer Chemistry*, Wiley, 12/year.
11. *Journal of Polymer Science, Part A-2, Polymer Physics*, Wiley, 12/year.
12. *Journal of Polymer Science, Part B, Polymer Letters*, Wiley, 12/year.
13. *Journal of Polymer Science, Part C, Polymer Symposia*, Wiley, irregular.
14. *Macromolecules*, ACS, 12/year.
15. (F.L.) *Die Makromolekulare Chemie*, Hüthig and Wepf Verlag, Basel, 10/year.
16. *Papers Presented*, Division of Organic Coatings and Plastics Chemistry, ACS, 2/year.
17. *Polymer*, Butterworths, London, 12/year.
18. *Polymer Degradation and Stability*, Applied Science Publishers, London, 4/year.
19. *Polymer Engineering and Science* (formerly *SPE Transactions*), Society of Plastics Engineers, 12/year.
20. *Polymer Journal*, Soc. of Polymer Science (Japan), 12/year.
21. *Polymer Mechanics* (English translation of Russian-language *Mekhanika Polimerov*), Faraday Press, New York, 12/year.
22. *Polymer News*, Gordon and Breach, 6/year.
23. *Polymer Preprints*, Division of Polymer Chemistry, ACS, 2/year.
24. *Polymer Science: USSR*, Pergamon, London, 12/year. (Cover-to-cover translation of Russian-language *Vysokomolekuliarnye Soedinenia*.)
25. *Proceedings of the Annual Technical Conference*, SPI Reinforced Plastics Division, 1/year.
26. *Rubber Chemistry and Technology*, Division of Rubber Chemistry, ACS, 5/year.
27. *Technical Papers*, Society of Plastics Engineers, Annual Technical Conference, 1/year.
28. *Textile Research Journal*, Textile Research Institute, 12/year.
29. *Transactions and Journal of the Plastics Institute*, The Plastics Institute, London.

30. *Transactions and Proceedings of Institute of the Rubber Industry*, IRI, London, 12/year.
- B. Journals that often report polymer work along with other fields. Many of these antedate those in category A, so much of the older literature of polymer science is found here.
 1. *Analytical Chemistry*, ACS.
 2. *ChemTech*, ACS.
 3. *Industrial and Engineering Chemistry Product Research and Development Quarterly* ACS.
 4. *Journal of the American Chemical Society*, ACS.
 5. *Journal of Applied Physics*, American Institute of Physics.
 6. *Journal of Chemical Physics*, American Institute of Physics.
 7. *Journal of Colloid Chemistry*, Academic Press.
 8. *Journal of Organic Chemistry*, ACS.
 9. (F.L.) *Rheologica Acta*, Steinkopff Verlag, Darmstadt.
 10. *Transactions of the Faraday Society*, The Faraday Society, London.
 11. *Transactions of the Society of Rheology*, The Society of Rheology.

A3-3 JOURNALS DEVOTED TO POLYMER TECHNOLOGY

These journals often emphasize a particular industry.

A. Journals primarily oriented toward polymers.

Adhesives

1. *Adhesives Age*, Communication Channels, 12/year.
2. *Journal of Adhesion*, Technomic, 4/year.

Coatings

3. *American Paint and Coatings Journal*, American Paint Journal Co., St. Louis, 12/year.
4. *Journal of the Oil and Colour Chemists Association*, London, 12/year.
5. *Journal of Coatings Technology* (formerly the Official Digest), Federation of Societies for Paint Technology, Philadelphia, 12/year.
6. *Modern Paint and Coatings* (formerly *Paint and Varnish Production*), Palmeton, 12/year.
7. *Paint Manufacture*, Wheatland, England, 10/year.
8. *Powder Coatings Bulletin*, Elsevier, 12/year.
9. *Progress in Organic Coatings*, Elsevier, 3/year.
10. *Waterborne and High Solids Coating Bulletin*, Elsevier, 12/year.

Elastomers

11. *British Plastics and Rubber*, Findlay (England), 12/year.
12. *Elastomerics* (formerly *Rubber Age*), Communication Channels, 12/year.
13. *European Rubber Journal*, Maclaren Publishers (England), 10/year.

14. *Journal of the IRI*, Institute of the Rubber Industry, London, 6/year.
15. *NR Technology*, Malaysian Rubber Producers' Research Assoc. (England), 4/year.
16. *Plastics and Rubber International*, Plastics and Rubber Institute (England), 6/year.
17. *Rubber and Plastics Age* (London), Rubber and Technical Press, 12/year.
18. *Rubber and Plastics News*, Crain Automotive Group, 26/year.
19. *Rubber Developments*, Natural Rubber Bureau, Washington, D.C., 12/year.
20. *Rubber World*, Bill, 12/year.
21. *Soviet Rubber Technology* (English translation of Russian-language *Kauchuk i Rezina*), Davis, Croydon, England, 12/year.

Fibers

22. *American Dyestuff Reporter*, Howes, 26/year.
23. *Canadian Textile Journal*, Canadian Textile Journal Publishing Co., Montreal, 26/year.
24. *Fibre Chemistry* (English translation of Russian-language *Khimicheskie Volokna*), Plenum, 6/year.
25. *Modern Textiles Magazine*, Rayon Publishers, 12/year.
26. *Textile Industries*, Smith, 12/year.
27. *Textile Month*, Textile Business Press, (England), 12/year.
28. *Textile Organon*, Textile Economics Bureau, 12/year.
29. *Textile World*, McGraw-Hill, 12/year.

Plastics and General Materials

30. *European Journal of Cellular Plastics*, Technomic, 5/year.
31. *European Plastics News*, Iliffe, 12/year.
32. *Insulation*, Lake, 12/year.
33. *Journal of Cellular Plastics*, Technomic, 6/year.
34. *Journal of Composite Materials*, Technomic, 4/year.
35. (F.L.) *Kunststoffe*, Carl Hanser Verlag, Munich, 12/year.
36. *Kunststoffe*—German Plastics (English translation), 12/year.
37. *Materials Engineering*, Reinhold, 12/year.
38. *Modern Plastics*, McGraw-Hill, 12/year.
39. *Plastics (London)*, Heywood-Temple, London, 12/year.
40. *Plastics Design and Processing*, Lake, 12/year.
41. *Plastics Engineering*, Soc. Plastics Engineers, 12/year.
42. *Plastics Technology*, Bill, 12/year.
43. *Plastics World*, Cahners, 12/year.
44. *Polymer Plastics Technology and Engineering*, Dekker, 4/year.
45. *Polymer Testing*, Applied Science Publ., London, 4/year.
46. *Reinforced Plastics and Composites World*, Cahners, 6/year.
47. *Soviet Plastics* (English translation of Russian-language *Plasticheskie Massy*), Rubber and Plastics Research Association, Shawbury, England, 12/year.

B. Journals that often report polymer work. Certain kinds of information such as production flow charts are more often found here than in any other category of literature.

48. *AIChE J.*, American Institute of Chemical Engineers, 6/year.

49. *Chemical Engineering*, McGraw-Hill, 26/year.

50. *Chemical and Engineering News*, ACS, 52/year.

51. *Chemical Engineering Progress*, American Institute of Chemical Engineers, 12/year.

52. *Chemical Week*, McGraw-Hill, 52/year.

53. *Hydrocarbon Processing*, Gulf, 12/year.

54. *Modern Packaging*, McGraw-Hill, 12/year.

A3-4 ABSTRACT AND BIBLIOGRAPHY SERVICES

In addition to those listed here, some specialized services are offered by consultants in specified fields.

1. *Applied Science and Technology Index*, H. W. Wilson, New York, 52/year.

2. *Bibliography of Rubber Literature*, 1924-, Division of Rubber Chemistry, ACS. A multi-volume, hardcover series with brief abstracts of articles. Usually issued about five years after date of coverage.

3. Bibliographies of selected subjects in rubber chemistry and fabrication. A list can be obtained from Division of Rubber Chem., ACS, Library and Information Service, University of Akron, Akron, Ohio.

4. *Chemical Abstracts*, ACS (macromolecular sections available separately), 26/year.

5. *Plastics Monthly* (the plastics section of the *Engineering Index*), Engineering Index Inc., 12/year.

6. *Quarterly Literature Reports: Polymers* (critical reviews of papers and patents), Academic Press, 4/year.

7. *Resins, Rubbers, Plastics Yearbook*, Information for Industry Inc., Washington, D.C., 1/year.

8. *Rheology Abstracts*, British Society of Rheology, Pergamon, 4/year.

9. *U.S. Government Research and Development Reports*, U.S. Dept. of Commerce, 24/year (esp. Field 7, Chemistry, and Field 11, Materials).

A3-5 BOOKS

A comprehensive list of books on polymer science was published by G. J. Patterson: "Plastics Book List," Technomic, Westport, Conn., 1975. Over 1600 books are classified under 40 headings. Each year in connection with the fall meeting of the American Chemical Society, the *Journal of Chemical Education* publishes, as part of their September issue, a list of new books with a separate category for polymers. In this book, general references have been included at the end of each chapter to relatively recent works in the field. Most of the journals listed in Secs. 2 and 3 carry reviews of new books in their areas of interest.

LABORATORY EXERCISES

There is great value in laboratory experience with polymers. Rubber, plastics, fibers, coatings, and adhesives are so much a part of our daily lives that many aspects of laboratory practice merely help to make quantitative what we already have seen in a qualitative sense. The experiments suggested here are confined to those that require little equipment beyond what ordinary physical and organic chemistry laboratories offer. Some pieces of apparatus can be fabricated easily. Also, experiments requiring only a few hours in the laboratory are emphasized.

The acquisition of commercial instruments rapidly expands the kinds of experiments to be attempted, especially in the areas of rheology, fabrication, and testing. Polymerization experiments often require less equipment but demand time in excess of the single afternoon contemplated for the projects outlined here.

Another kind of project involves making models of polymers. Stereoregular models and their arrangement in helices can be represented by various means that have been described in *J. Chem. Ed.*, 45:507 (1968). The extension of some of the polarized light experiments (Exps. 10 and 11) into lecture demonstrations has been described in *J. Chem. Ed.*, 46:456 (1969).

Some sources of information on laboratory practice with polymers are listed below.

Polymerization

- G. F. D'Alelio, "Experimental Plastics and Synthetic Resins," Wiley, New York, 1946.
W. R. Sorenson and T. W. Campbell, "Preparative Methods of Polymer Chemistry," 2d ed., Interscience, New York, 1968.
S. H. Pinner, "A Practical Course in Polymer Chemistry," Pergamon, New York, 1961.
E. L. McCaffery, "Laboratory Preparation for Macromolecular Chemistry," McGraw-Hill, New York, 1970.

- D. Braun, H. Cherdon, and W. Kern, "Techniques of Polymer Synthesis and Characterization," Wiley, New York, 1971.
- E. A. Collins, Jan Bareš, and F. W. Billmeyer, Jr., "Experiments in Polymer Science," Wiley, New York, 1973.

Rheology (the study of the flow and deformation of matter)

- J. R. Van Wazer, J. W. Lyons, K. Y. Kim, and R. E. Colwell, "Viscosity and Flow Measurement," Interscience, New York, 1963.
- D. M. Best and S. L. Rosen, A Simple, Versatile and Inexpensive Rheometer for Polymer Melts, *Polymer Eng. Sci.*, 8:116 (1968).
- F. Rodriguez and A. J. Berger, in *Proc. 4th Intl. Cong. Rheology*, part 3, p. 41, E. H. Lee (ed.), Interscience, New York, 1963. Simple viscometer for non-Newtonian flow.

Microscopy

- E. M. Chamot and C. W. Mason, "Handbook of Chemical Microscopy," vol. 1, 3d ed., Wiley, New York, 1958.
- J. L. Stoves, "Fibre Microscopy," National Trade Press, 1957.
- S. B. Newman, Microscopy in "Analytical Chemistry of Polymers," part 3, G. M. Kline (ed.), Interscience, New York, 1962.

Elementary Safety Precautions

1. Know the properties of the materials with which you will be working *before* entering the laboratory.
2. Acrylamide, ethyl acrylate, and most monomers and peroxides are poisons. Inhalation, ingestion, and contact with skin or eyes are to be avoided. Always work with adequate ventilation.
3. Safety glasses must be worn when dealing with any potentially hazardous situation such as stirred or heated vessels, physical testing machinery, or chemical reactions.
4. Smoking should not be permitted in the laboratory.

Experiment 1 Adiabatic Solution Polymerization of Acrylamide

Acrylamide is a crystalline solid melting at 84.5°C. The solid is quite stable, although ionizing radiation can cause polymerization. However, in bulk or in solution, the monomer is unstable at higher temperatures, especially if oxygen is completely absent. The polymerization is carried out conveniently in aqueous solution using a persulfate initiator at 50 to 70°C, or near room temperature when a reducing agent such as a bisulfite is added to accelerate the generation of free radicals.

Materials

		Molecular weight
1. Acrylamide	$\text{CH}_2=\text{CH}-\text{CO}-\text{NH}_2$	71.08
2. Potassium persulfate	$\text{K}_2\text{S}_2\text{O}_8$	270.33
3. Sodium metabisulfite	$\text{Na}_2\text{S}_2\text{O}_5$	190.11

Equipment

Dewar flask (one quart) *A*, with stirrer *B*, thermometer *C*, nitrogen inlet *D*, and port for addition of solutions *E* (Fig. A4-1*a*)

Polymerization

1. Dissolve acrylamide (20 g) in distilled water (400 ml) and place in Dewar flask. Sparge with nitrogen for 5 min.
2. Add 5 ml of a 5 wt % solution of persulfate from a syringe. Thirty seconds later, add 5 ml of a 5 wt % solution of metabisulfite. Stop nitrogen flow.
3. Record temperature vs. time until the temperature goes through a maximum.
4. Stop agitation. The solution may be saved for measurement of intrinsic viscosity. About 10 ml of solution can be evaporated in an aluminum dish in order to observe the properties of the solid polymer.

Report

1. Plot temperature vs. time.
2. Calculate the heat of polymerization for acrylamide (kcal/mol) assuming (*a*) complete conversion, (*b*) specific heat of monomer and polymer is $0.5 \text{ cal/g}\cdot^\circ\text{C}$, and (*c*) specific heat of water is $1.0 \text{ cal/g}\cdot^\circ\text{C}$.
3. Describe the appearance of the dry polymer.

Experiment 2 Photosensitized Solution Polymerization of Acrylamide

Ultraviolet light will interact with many compounds to generate free radicals, which in turn will initiate free-radical polymerization. The system described here is somewhat unusual in that visible light is sufficient to generate the radicals and oxygen (dissolved air) is actually needed to make the reaction go.¹

Materials

1. Acrylamide (see Exp. 1)
2. Riboflavin-5'-phosphate, sodium

¹ The present system was described by G. Oster in *Nature*, 173:300, Feb. 13, 1954, and *J. ACS*, 79:595 (1957). A more elaborate and up-to-date summary of acrylamide photopolymerization is that of C. S. H. Chen in "Photopolymers—Principles, Processes, and Materials," Mid-Hudson Section of Society of Plastics Engineers, 1967.

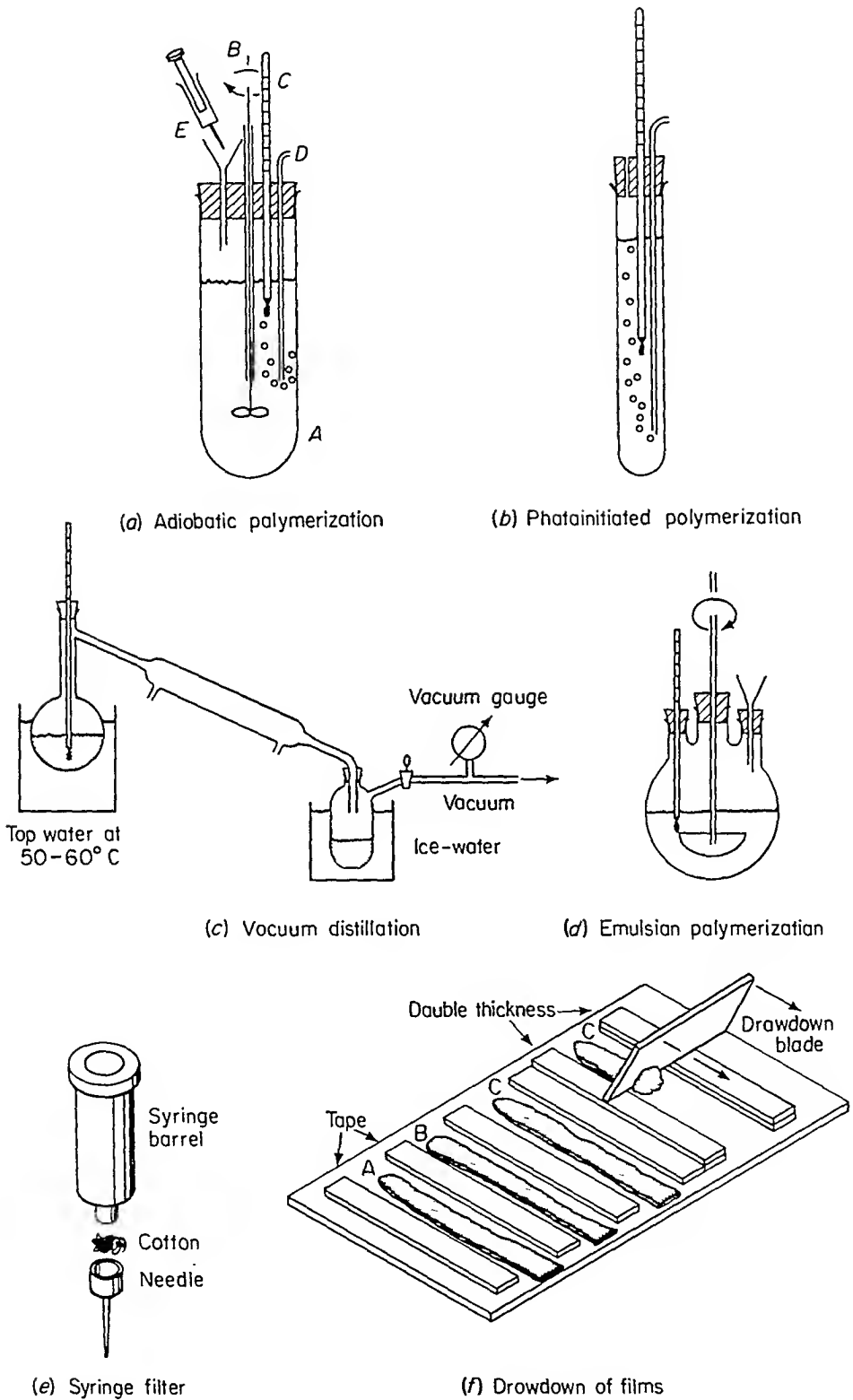


FIGURE A4-1
Examples of experimental apparatus (Exps. 1 through 7).

Equipment

Test tubes (20 × 150 mm) with thermometers and gas-inlet tubes (Fig. A4-1*b*)

Polymerization

1. Five test tubes are fitted with thermometers centered by means of loose-fitting corks. They each are filled with 25 ml of a 40 wt % solution of acrylamide in distilled water. To each is added (*a*) 1 ml of water, (*b*) 0.8 ml water, 0.2 ml of a 0.1 wt % solution of riboflavin, (*c*), (*d*), and (*e*), 1.0 ml of the 0.1 wt % solution of riboflavin.
2. Tubes *a* through *d* are placed in a rack where they can be illuminated by the light from an ordinary slide projector (300 or 500 W at a distance of about 3 ft). Tube *e* is placed at twice the distance from the light source. Nitrogen is bubbled through tube *d*.
3. With the tubes in place and nitrogen bubbling through tube *d*, illuminate and record temperature as a function of time.

Report

1. Plot temperature for all test tubes vs. time up to the time that the temperature for tube *e* goes through a maximum.
2. What do you expect the rate of radical generation to be in tubes *a*, *b*, *d*, and *e* relative to the rate in tube *c*?
3. Did monomer in solution, but hidden from the projector, polymerize?

Experiment 3 Emulsion Polymerization of Ethyl Acrylate

Ethyl acrylate is a liquid boiling at 99.5°C. Commercially it is shipped with varying amounts of a polymerization inhibitor, 0.02 to 0.10 wt % hydroquinone being typical. The inhibitor level can be reduced to a negligible level by vacuum distillation or extraction by alkali. A redox couple is used to initiate polymerization at room temperature.

Materials

		Molecular weight
1. Ethyl acrylate	$\text{CH}_2=\text{CH}-\text{CO}-\text{O}-\text{CH}_2\text{CH}_3$	100.1
2. Sodium lauryl sulfate	$\text{Na}-\text{O}-\text{SO}_2-\text{O}-(\text{CH}_2)_{11}\text{CH}_3$	285
3. Potassium persulfate	see Exp. 1	
4. Sodium metabisulfite	see Exp. 1	
5. Ferrous sulfate	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	278

Equipment

1. Vacuum distillation equipment (Fig. A4-1*c*)
2. Separatory funnel

3. Three-necked, round-bottom flask with thermometer and stirrer (Fig. A4-1d) or Dewar flask of Exp. 1

Inhibitor Removal

1. Vacuum-distill about 100 ml of monomer from a charge of 130 ml. Store distilled monomer in ice water. *Do not pour ethyl acrylate down the sink.*
2. If vacuum distillation is not practical, wash 100 ml of monomer in the separatory funnel with 20 ml of a 5% NaOH solution saturated with NaCl. Wash subsequently with three successive portions of saturated NaCl aqueous solution.

Polymerization

1. Charge 300 ml of distilled water to the reactor and sparge with nitrogen for 5 min with stirring.
2. Stop nitrogen flow and add 10 ml of a 10% solution of surfactant.
3. With continued stirring, add 80 ml of monomer.
4. Add 5 ml of a 5 wt % solution of persulfate. Thirty seconds later, add 5 ml of a 5 wt % solution of bisulfite. After an additional 30 s add 1 ml of a 1 wt % solution of ferrous sulfate.
5. Record the temperature as a function of time until 5 min after the temperature goes through a maximum.

Polymer Recovery

1. Coagulate 50-ml aliquots of the latex by addition of:

Methanol	5% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$
5% NaCl	5% $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$

2. Record the volume of each needed for coagulation. After washing thoroughly with water, dry (100°F air oven) and weigh the yield from each aliquot.
3. Coagulate the balance of the latex with $\text{Al}_2(\text{SO}_4)_3$ solution and wash thoroughly with water. Dry the coagulum (100°F air oven) and calculate the total yield based on monomer charged.

Report

1. Plot temperature vs. time.
2. Estimate the heat of polymerization. See Exp. 1.
3. Summarize the experiments on coagulation.
4. Convert the experimental value of $dT/d\theta$, rate of temperature rise, to $dM/d\theta$, the rate of monomer conversion.
5. Report the yield.

Experiment 4 Intrinsic Viscosity

Viscosity measurement is by far the most popular method for characterizing the molecular size of polymers. It is a relative method which must be calibrated by some

absolute method such as osmometry or light scattering. Even without such calibration, dilute solution viscosity is a useful tool for preliminary examination of laboratory preparations and for routine control of production processes.

Materials

Solution of polyacrylamide in water from Exp. 1

Equipment

1. Ubbelohde viscometer, flow time for water at least 80 s
2. 10-ml syringe
3. Pipettes, 1 and 5 ml
4. Constant-temperature bath at 30°C

Procedure

1. Bring polymer concentration to 2 g/dl.
2. Using a plug of cotton as a filter (Fig. A4-1e) pull a little more than the minimum amount of polymer solution to operate the viscometer into the syringe. Remove needle and plug.
3. Weigh the full syringe to the nearest milligram, eject the contents into the viscometer, and reweigh the syringe immediately.
4. After about 5 min of temperature equilibration in the bath, time the flow of polymer out of the upper bulb several times. Agreement should be at least within 0.5% for successive flow measurements.
5. Add water from pipettes to dilute the solution to three-fourths of its initial concentration, mix, equilibrate, and measure flow time.
6. Repeat step 5 two more times.

Report

1. Calculate concentrations and convert flow times to viscosity using an equation of the form of (7-5).
2. Plot data according to Eqs. (7-13) and (7-14).
3. Estimate $[\eta]$, k' , and k'' .
4. For the system polyacrylamide-water¹ at 30°C

$$[\eta] = 6.8 \times 10^{-4} (M)^{0.66}$$

For water, 30°C,

$$\eta = 0.8004 \text{ centipoise} \quad \rho = 0.9956 \text{ g/cm}^3$$

Calculate the viscosity-average molecular weight.

¹E. Collinson et al., *Trans. Faraday Soc.*, 53:489 (1957).

5. If a new sample of polymer exhibited the same flow time as your sample did before dilution, but at two-thirds the concentration, what would you estimate for M_v ?

Experiment 5 Film Formation from Linseed Oil

The drying of an unsaturated oil is a complex process in which peroxides and hydroperoxides form and decompose. Linseed oil is recovered from flaxseeds by pressing and solvent extraction. It is a partially unsaturated triglyceride (see Sec. 12-4).

Materials

1. Raw linseed oil
2. Solvent (mineral spirits or petroleum ether)
3. Cobalt solution (cobalt soap of naphthenic acids, 6% Co)

Equipment (Fig. A4-1f)

1. Glass panel about 9 by 12 in
2. Drawdown blade (straight-edged, metal)

Procedure

1. Make up the following solutions (parts by weight):

	<i>A</i>	<i>B</i>	<i>C</i>
Linseed oil	100	100	100
Solvent	100	100	100
Cobalt metal	—	0.02	0.05

2. On a pane of glass about 9 by $\frac{1}{2}$ in, lay out four channels using cellophane tape as indicated in Fig. A4-1f.
3. Draw down films of each as indicated in Fig. A4-1f.
4. Observe, by touching at $\frac{1}{2}$ -h intervals, the change in each film through wet, tacky, and dry stages. Although automatic devices can be used, a simple criterion for dryness involves dropping a tuft of cotton on the film. If the cotton falls off when the film is inverted, the film is dry.

Report

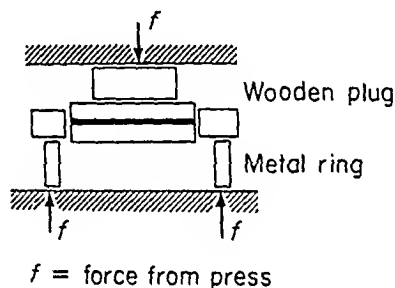
1. Time for each film to pass through various stages of dryness. (It may be necessary to examine the film at long intervals over several days.)
2. Would the films dry faster (a) at higher temperatures, (b) at lower humidities, or (c) with pigment added?

Experiment 6 Compression Molding

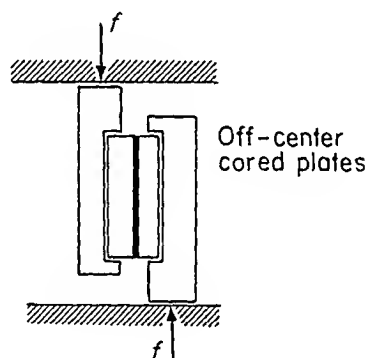
An elementary compression mold can be made from a ring and two plates (about 4 in in diameter) (Fig. 12-29). In a commercial machine the upper and lower plates move with guidance provided by a system of sliding rods. In this mold, however, the mold ring, with a clearance of about 0.002 in in diameter, acts as a guide, while an external press provides the pressure and heat. In a full-sized press the mold parts are separated after molding because they are fastened to the platens of the main press. Here we resort to an extraction assembly and a breaker subassembly (Fig. A4-2*a* and *b*) in order to use the press in compression again.

Materials

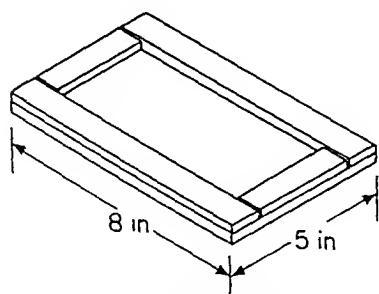
1. A thermosetting phenolic resin (commercial grade)
2. A thermoplastic molding resin [commercial pellets of polyethylene, polystyrene, or poly(methacrylate) will do]
3. Silicone mold release (spray can)



(a) Extraction assembly

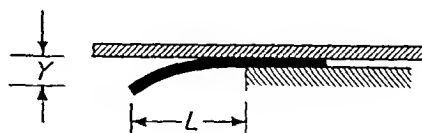


(b) Mold "breaking" assembly



Aluminum strips, 1 x 1/16 in glued onto aluminum plate with commercial epoxy resin

(c) Flat-plate mold for cast plastics



(d) Measurement of modulus

FIGURE A4-2

Examples of experimental apparatus (Exps. 6 through 8).

Equipment

1. Ring-and-plate mold with extraction and breaker assemblies (Fig. A4-2)
2. A laboratory press with electrically heated platens and provision for circulating cooling water

Typical Procedure for a Phenolic Resin (Plenco 411 Walnut Mottle)¹

1. After spraying mold surfaces lightly with silicone oil, preheat them to 155°C in the press. Allow 5 min.
2. With base plate in mold ring, add 20 g of resin powder, start timer.
3. Quickly put plunger in position and close press. At 30 s from start of timer, pressure should be 5000 lbf. At 60 s from start, increase pressure to 20,000 lbf. This can be increased gradually over a period of 30 s if too much material is being squeezed out.
4. Hold pressure at 18 to 20,000 lbf for 10 min.
5. Open the press, extract plunger, molding, and plate; then break apart molding from plate and plunger. Use insulated gloves.

Typical Procedure for a Branched Polyethylene of Melt Index 2 to 4

1. After spraying mold surfaces lightly with silicone oil, preheat them to 155°C.
2. Add 20 g of molding pellets with base plate in place and start timer.
3. Put plunger in position and close press. Slowly increase pressure until there is little tendency to lose pressure, but not so much that polymer extrudes around the periphery of the mold. Record time and pressure.
4. After holding 2 min, turn off heating elements and start cooling with circulating water.
5. When platen temperature reaches 50°C, stop water flow.
6. Extract molding as with thermoset.

Report

1. Describe the materials used in the experiment along with the manufacturer's specifications and molding recommendations.
2. Summarize the actual time-temperature-pressure cycles used.
3. Are there any advantages to compression molding over injection molding for thermoplastics?

Experiment 7 Casting Plastics

Emulsion-polymerized poly(vinyl chloride) is available commercially in a form that can readily be suspended in viscous liquids. Such paste, stir-in, or dispersion resins can be used to illustrate the need for heat stabilizers in this resin and the versatility imparted by plasticization.

¹Plastics Engineering Company, Sheboygan.

Materials

1. Plastisol resin powder
2. Plasticizer (di-2-ethylhexyl phthalate, or others such as adipates, phosphates, or sebacates)
3. A liquid epoxy resin (Epon 828, Shell, or others)
4. A liquid barium-cadmium stabilizer (commercial product) or dibutyl tin dilaurate

Equipment

1. Disposable aluminum weighing dishes
2. Flat plate molds (Fig. A4-2c)
3. Air-circulating oven

Heat Stability Test

1. Mix 50 g of resin with 35 of plasticizer; then pour 8.5-g portions into aluminum dishes.
2. Add to the first three dishes, 1 g each of plasticizer. Add to the second three dishes, 1 g of epoxy compound. Add to the third three 0.5 g each of plasticizer and stabilizer.
3. Place all nine samples in oven at 180°C. Remove dishes according to the following schedule:

Set 1 (no stabilizer)	5, 15, 30 min
Set 2 (epoxy)	15, 45, 75 min
Set 3 (stabilizer)	15, 45, 75 min

Report on Heat Stability

Prepare a heat stability chart on white paper as follows:

<i>Formulation</i>				
No stabilizer	(Staple 1 cm ² squares of actual test samples at proper coordinates)			
Epoxy stabilizer				
Metallic stabilizer				
	0	25	50	75
<i>Time at 180°C, min</i>				

Variable Plasticizer Test

1. Make up the following master batch:

Resin	100
Plasticizer	60
Metallic stabilizer	5
	165 g

2. To 33-g portions of the master batch add (and stir well): (a) no addition, (b) 4 g of plasticizer, (c) 8 g of plasticizer, and (d) 12 g of plasticizer.
3. Pour each batch into a flat mold (Fig. A4-2c) (after spraying each mold with silicone mold release) and place in air circulating oven for 15 min at 180°C.
4. Remove molds from oven and cool by immersing in water.
5. Remove plastic sheets from molds and store for modulus test.

Experiment 8 Measuring Modulus

As indicated in Chap. 8, the modulus of a polymeric material may be measured as a function of time, at equilibrium, or in some dynamic situation involving oscillations. Experiments in tension, compression, flexure, and torsion are convenient depending on geometry and stability of the specimen.

Materials

1. Strips of plasticized poly(vinyl chloride) from Exp. 7. Each strip should be about 4 to 6 in long and about $\frac{1}{2}$ in wide.
2. Strips of glassy plastics such as cellulose acetate or poly(methyl methacrylate).

Equipment

Ruler marked off in centimeters or decimal inches. A cathetometer allows the reading of deflection to a much greater degree of precision, but the experiment can be done without it.

Cantilever Beam Deflection

1. Support each strip as a cantilever beam from the edge of a table or book (Fig. A4-2d).
2. Measure the vertical deflection Y of the beam end after a waiting period of 10 s.
3. Measure Y in the range of 0.1 to 0.5 in for four values of beam length L .
4. Calculate the modulus E for each sample. For a cantilever beam of density ρ deformed under its own weight, the deflection Y is given by

$$Y = \frac{3\rho L^4}{2Ea^2}$$

Example

$$\rho = 80.0 \text{ lb/ft}^3 = 1.281 \text{ g/cm}^3$$

$$L = 1.00 \text{ ft} = 30.28 \text{ cm}$$

$$a = 0.125 \text{ in} = 0.3175 \text{ cm}$$

$$E = 5.00 \times 10^5 \text{ psi} = 3.447 \times 10^{10} \text{ dyn/cm}^2 \text{ (} 3.52 \times 10^7 \text{ g/cm}^2 \text{)}$$

$$Y = 0.184 \text{ in} = 0.468 \text{ cm}$$

Report

1. Plot Y versus L^4 and establish an average slope for each sample.
2. Plot E versus plasticizer content for the poly(vinyl chloride) samples.
3. Report E values for other materials measured and compare with literature values.
4. How would the modulus-plasticizer content plot be changed if E had been measured at a higher temperature or if more than 10 s had been allowed for each measurement?

Experiment 9 Rubber Elasticity

Ten gum-rubber bands are selected from a commercial assortment so as to be nearly equal in dimensions. Each band (2 to 5 in in total perimeter) is weighed to the nearest 0.1 mg. The average cross-sectional area is measured.

Swelling and Extraction

1. The bands are treated in the following manner at room temperature:

Bands	Placed in
1 to 4	<i>n</i> -Heptane
5 to 7	Mixture of <i>n</i> -heptane: mineral oil, 3:1
8 to 10	Mixture of <i>n</i> -heptane: mineral oil, 1:1

2. After 24 h the bands are removed and allowed to air-dry at room temperature for 2 days in a well-ventilated area. Bands 1 through 4 should also be weighed before drying. This is done by transferring them to a stoppered weighing bottle.
3. The bands are reweighed. The concentration of oil in the samples is calculated assuming that the same amount of material has been extracted as in the oilfree samples. Calculate also the volume fraction of rubber v_2 for the oilfree bands in *n*-heptane. Use the dried weight and the densities of rubber and *n*-heptane assuming additivity in the swollen state.

Elasticity

1. Record the length of each rubber band as weights are added and then removed in tension. Allow 10 s after each weight is added or removed. Add the weights in even increments so as to give about 8 to 10 steps in reaching 100% elongation.
2. It is sufficient to make the measurement on only one of each of the three types of treated bands.

Report

1. Plot stress vs. strain for each. From the plot measure the ratio of the energy lost to the total energy added (ratio of area of loop to area under original stress-strain curve).

2. Tabulate energy loss vs. oil content.
3. Plot the average value of stress and strain for each type of treated band in the manner of Fig. 8-3.
4. Calculate the chain density.
5. Calculate the solvent-polymer interaction parameter for the rubber band in *n*-heptane.

Experiment 10 Orientation of Amorphous Polymers in Polarized Light

An ordinary beam of light is a wave phenomenon vibrating equally in all directions around the axis of the beam. Certain anisotropic materials have the property of transmitting the component of light that vibrates perpendicular to that direction. Such a material, appropriately tailored in properties and geometry, becomes a polarizer so that the light that passes through it emerges vibrating in only one plane. The plane contains the axis of the beam and also the *vibration axis* of the polarizer.

Of course, if a second sheet of the same polarizing material intercepts the polarized light beam, it will transmit the light if the second sheet is oriented parallel to the first one. If the second sheet is rotated 90° , no light will pass. The second sheet in this crossed position is called an *analyzer*.

Now consider a specimen placed between the crossed sheets. If the specimen transmits light faster along one specimen direction than along another, the light from the polarizer will be split into two components by the specimen and enter the analyzer as two waves out of phase with each other. Such behavior is called *optical anisotropy*, *birefringence*, or *double refraction*. The mutually perpendicular, out-of-phase components of light emerging from the specimen appear bright when seen through the analyzer, since the light no longer vibrates exclusively in the plane perpendicular to the analyzer axis. The specimen will appear dark when its vibration axes coincide with the plane of vibration of the polarizer or analyzer. The specimen will appear brightest when its vibration axes are at an angle of 45° to the plane of vibration of the polarizer or analyzer.

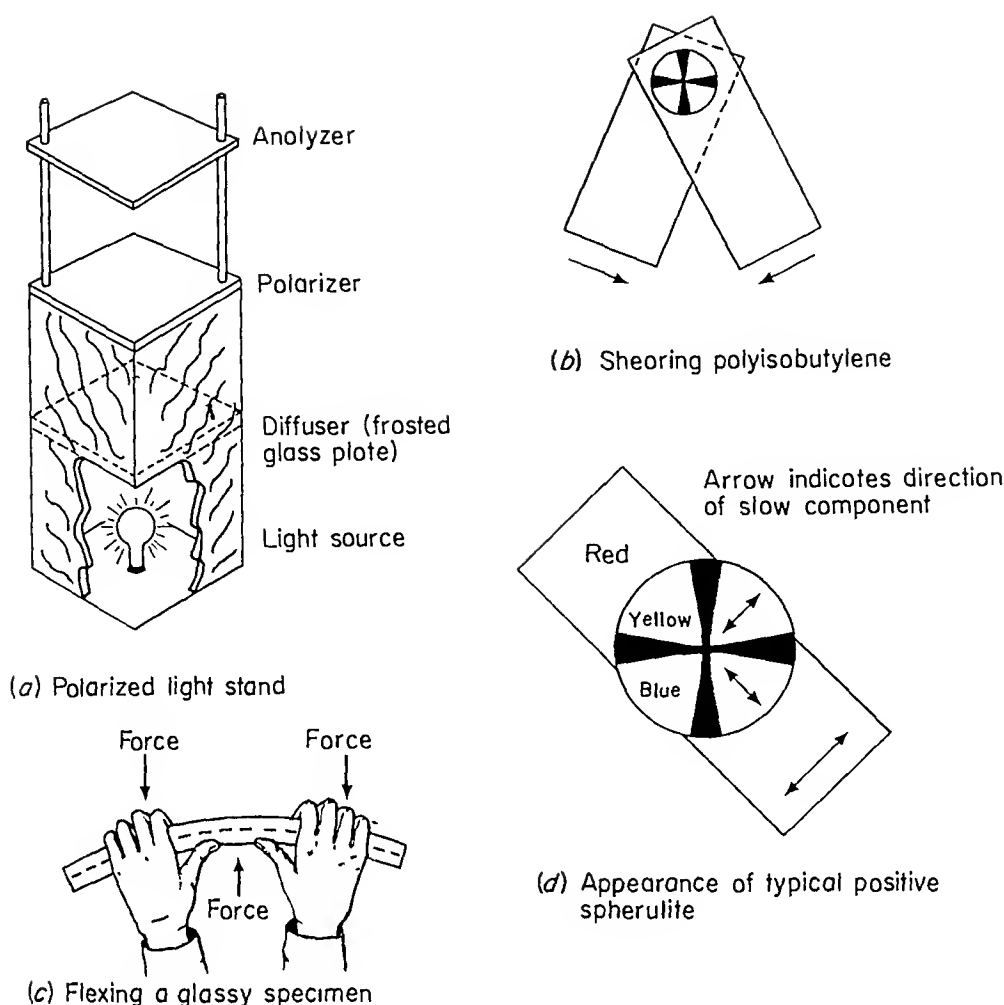
Materials

1. Polyisobutylene (Vistanex LM-MH)¹
2. Strips of raw and cross-linked rubber, transparent, about 0.01 to 0.1 in thick
3. Strip of commercial poly(methyl methacrylate), 12 by $\frac{1}{2}$ by $\frac{1}{8}$ in
4. Transparent injection-molded objects such as protractors, box lids, cups, etc., especially those made of polystyrene

Equipment

1. Two acrylic plastic sheets, about 6 by 2 by $\frac{1}{8}$ in
2. Two sheets of polarizing material, about 6 by 6 in or larger. They should be mounted above one another with diffused light below and working space in between the sheets (Fig. A4-3a).

¹ Enjay Chemical Co., New York.

**FIGURE A4-3**

Examples of experimental apparatus (Exps. 10 and 11).

3. A first-order red plate, about 6 by 1 in. Often this can be approximated by strips of clear cellophane or cellophane tape or cellulose acetate.

Orientation at Large Strains

1. About 1 g of low-molecular-weight polyisobutylene is squeezed between the two acrylic sheets to give a disc about an inch in diameter and about $\frac{1}{16}$ in thick.
2. With the sandwich of acrylic sheets and polyisobutylene between the crossed polarizing sheets, shear the sample by rotating the top sheet around an axis through the center of the disc. Observe the maltese cross that appears (Fig. A4-3b).
3. How much recoil takes place if rotation of the top sheet is stopped suddenly? How fast does the cross pattern disappear?
4. If rotation is stopped but the sheets held in fixed position without allowing recoil, how long does it take for the cross to disappear?

Report

1. Record observations under 3 and 4 of the preceding section.
2. How are the polymer molecules oriented in the polymer during shearing?

Effect of Molecular Weight on Relaxation Time

1. Stretch strips of raw and cross-linked rubber between crossed polarizers. Observe the changes in pattern as the sample under tension is rotated with respect to the plane of vibration of the polarizer.
2. Observe and record the time it takes for the birefringence pattern to disappear when the sample is held at a fixed strain. Record the permanent changes in dimensions of the samples used after stretching.

Report

1. Compare the time for the birefringence pattern to disappear (relaxation at fixed strain) for the samples which vary in molecular weight.
2. Report the permanent changes in dimensions for raw vs. cross-linked rubber. How does the Maxwell model (Chap. 8) correspond to the behavior of these materials?

Use of a First-Order Red Plate

As the difference in index of refraction between two mutually perpendicular directions in the specimen increases or as the sample thickness increases, colors are observed between crossed polarizers. White, yellow, red, blue, and green appear successively, and then the cycle repeats with yellow, red, blue, green, etc. (see reference to Chamot and Mason in introduction to this appendix for a chart showing the relationship between birefringence, thickness, and color).

If one superimposes on the specimen a test plate which itself is a birefringent material for which the direction of higher refractive index is known, the change in color will indicate the direction of higher refractive index in the specimen. Conventionally, first-order red plates are rectangular with the short side corresponding to the direction of higher refractive index (slow component of light). If a low-order polarization color in a specimen is increased in order by superposition of the first-order red plate, then the higher refractive index is in the same direction in the specimen as in the plate. A first-order white combined with the red gives blue. If the directions of higher refractive index in specimen and plate are crossed, the red is partially *compensated* and a yellow color is seen.

Sign of Elongation

When a piece of rubber is stretched, or when a specimen with a long axis is examined, the sign of elongation is said to be positive if the slow component of light vibrates approximately parallel to the long direction of the specimen.

Repeat the preceding experiments with polyisobutylene in shear and rubber in tension using a first-order red plate to determine the sign of elongation.

Stress Birefringence

The large-scale deformation of rubber results in birefringence because of the uncoiling of flexible molecules. The flexibility comes from relatively free rotation about single bonds. In a glass, stress is stored by bond bending and stretching. Electron configura-

tions in these bonds are distorted by high stresses in the glass even though the strain may be small, say on the order of 1% or so.

1. A strip of acrylic plastic, 12 by $\frac{1}{2}$ by $\frac{1}{8}$ in, is stressed in flexure (Fig. A4-3c) between crossed polarizers. Record the maximum fiber strain imposed. The maximum fiber strain ϵ_m is $4bY/L^2$ for a beam of width b and length L that is deflected at its center a distance Y .
2. Repeat with a first-order red plate. What is the sign of elongation?
3. Observe an injection-molded article between crossed polarizers (a polystyrene protractor will do).

Report

1. When the acrylic strip is flexed, why does the center of the strip remain dark?
2. Do the patterns in the injection-molded article represent bond bending and stretching or chain uncoiling?
3. Draw a diagram of the protractor (or other article) indicating the direction of flow of plastic during molding as indicated by the residual birefringence.

Experiment 11 Crystalline Materials in Polarized Light

When a spherulite is observed in two dimensions, it has radial symmetry. Since orientation occurs in the crystallites making up the spherulite, there will be an overall orientation in the spherulite. If one knows the sign of elongation for the polymer in the rubbery state, a first-order red plate can be used to test the orientation of polymer molecules in the spherulite. A *positive spherulite* is one in which the slow component of light is oriented radially and the fast component tangentially (Fig. A4-3d).

Materials

1. Low-molecular-weight poly(ethylene oxide), Carbowax 4000¹
2. Low-density polyethylene film (about 0.001 in thick)

Equipment

Same as Exp. 10

Spherulite Growth

1. At 70 to 100°C, squeeze out about 0.1 g of poly(ethylene oxide) between two glass plates. Lantern slide covers, $3\frac{1}{4}$ by 4 in, are suitable. Cellophane tape strips can be used as spacers.
2. Cool slowly between crossed polarizers. If the temperature can be maintained at about 45 to 50°C, large spherulites are obtained. Observe the number of nuclei in some small area (about 1 cm²) and the rate of radial growth.
3. Use a first-order red plate to obtain the sign of the spherulites.

¹Union Carbide Corp., New York.

4. If it is possible, use a high-molecular-weight sample of poly(ethylene oxide) in tension above its T_m to obtain the sign of elongation.

Report

1. Report the largest spherulite radius obtained, the approximate number of nuclei per square centimeter, and the approximate rate of radial growth at the crystallization temperature used.
2. Report the sign of the spherulites, the sign of elongation, and the orientation of molecules in the spherulite.

Spherulitic Instability on Stressing

1. Stretch a dumbbell or strip of the thin polyethylene film between crossed polarizers. Observe the reversibility of the colors formed at various stages of strain.
2. When a large permanent elongation has been applied, try tearing the strip down the center.

Report

1. Are the reversible polarization colors observed at very low stresses due to bond bending and stretching or to chain uncoiling? What about the colors that appear permanent at high elongations?
2. Report the *draw ratio*, the ratio of final length to initial length of material in the neck region.

APPENDIX

5

SELECTED PROPERTIES
OF POLYMER SYSTEMS

TABLE A5-1
Typical Properties* of Polymers Used for Molding and Extrusion†

	ASTM test method	ABS medium impact	Acetal	Cellulose acetate
Specific gravity	D792	1.03 to 1.06	1.42	1.22 to 1.34
Refractive index	D542	—	1.48	1.46 to 1.50
Tensile strength, psi $\times 10^{-3}$ *	D638, D651	6 to 7.5	9.5 to 12	1.9 to 9.0
Elongation, %	D638	5 to 25	25 to 75	6 to 70
Tensile modulus, psi $\times 10^{-5}$	D638	3 to 4	5.2	0.65 to 4.0
Compressive strength, psi $\times 10^{-3}$	D695	10.5 to 12.5	18	3 to 8
Flexural yield strength, psi $\times 10^{-3}$	D790	11 to 13	14	2 to 16
Impact strength, notched Izod, ft·lb/in	D256	3 to 6	1.3 to 2.3	1 to 7.8
Hardness, Rockwell	D785	R107 to 115	M94 to R120	R34 to 125
Flexural modulus, psi $\times 10^{-5}$	D790	3.7 to 4.0	3.8 to 4.3	—
Compressive modulus, psi $\times 10^{-5}$	D695	2.0 to 4.5	6.7	—
Thermal conduct., (cal/s·cm·K) $\times 10^4$	C177	4.5 to 8.0	5.5	4 to 8
Specific heat, cal/g·K	...	0.3 to 0.4	0.35	0.3 to 0.4
Linear therm. exp. coeff., K ⁻¹ $\times 10^4$	D696	8 to 10	10	8 to 18
Continuous use temperature, °C	...	71 to 93	90	60 to 105
Deflection temp., °C at 0.45 MPa	D648	102 to 107	124	50 to 100
Volume resistivity, ohm·cm	D257	2.7×10^{16}	1.0×10^{15}	10^{10} to 10^{14}
Dielectric strength, kV/in	D149	350 to 500	500	250 to 500
Dielectric constant at 1 kHz	D150	2.4 to 4.5	3.7	3.4 to 7.0
Dissipation factor at 1 kHz	D150	0.004 to 0.007	0.004	0.01 to 0.07
Deleterious media	D543	Conc. oxidizing acids, organic solvents	Strong acids, some other acids and bases	Strong acids and bases
Solvents (room temperature) (Cl.H. = chlorinated hydrocarbons)	...	Ketones, esters, some Cl.H.	None	Ketones, esters, Cl.H.

*Conversion factors: 1000 psi = 6.895 MPa; 1 ft·lb/in = 53.4 J/m; 1 cal = 4.187 J; 1 kV/in = 0.0394 MV/m.

†Based on data from *Modern Plastics Encyclopedia*.

Cellulose acetate-butyrate	Cast epoxy glass fiber fill	Fluoro polymers		Ionomers
		$-\text{CF}_2\text{CFCl}-$	$-\text{CF}_2\text{CF}_2-$	
1.15 to 1.22	1.6 to 2.0	2.1 to 2.2	2.14 to 2.20	0.93 to 0.96
1.46 to 1.49	—	1.425	1.35	1.51
2.6 to 6.9	5 to 20	4.5 to 6	2 to 5	3.5 to 5.0
40 to 88	4	80 to 250	200 to 400	350 to 450
0.5 to 2.0	30	1.5 to 3	0.58	0.2 to 0.6
2.1 to 7.5	18 to 40	4.6 to 7.4	1.7	—
1.8 to 9.3	8 to 30	7.4 to 9.3	—	—
1 to 11	0.3 to 10	2.5 to 2.7	3.0	6.0 to 15
R31 to 116	M100 to 112	R75 to 95	D50 to 55 (Shore)	D50 to 65 (Shore)
—	20 to 45	—	—	—
—	—	—	—	—
4 to 8	4 to 10	4.7 to 5.3	6.0	5.8
0.3 to 0.4	0.19	0.22	0.25	0.55
11 to 17	1 to 5	4.5 to 7	10	12
60 to 105	150 to 260	175 to 200	290	70 to 95
54 to 108	—	126	121	38
10^{11} to 10^{15}	Over 10^{14}	1.2×10^{18}	Over 10^{18}	Over 10^{16}
250 to 400	300 to 400	500 to 600	480	900 to 1100
3.4 to 6.4	3.5 to 5.0	2.3 to 2.7	Under 2.1	2.4
0.01 to 0.04	0.01	0.023 to 0.027	Under 0.0002	0.0015
Strong acids and bases	None	None	None	Acids, esp. strong, oxidizing acids
Ketones, esters, Cl.H.	None	Swells in Cl.H.	None	None

TABLE A5-1
Typical Properties* of Polymers Used for Molding and Extrusion† (Continued)

	ASTM test method	Melamine- formaldehyde (cellulose fill)	Nylon 66 (moisture- conditioned)	Nylon 6 (moisture- conditioned)
Specific gravity	D792	1.47 to 1.52	1.13 to 1.15	1.12 to 1.14
Refractive index	D542	—	1.53	—
Tensile strength, psi $\times 10^{-3}$	D638, D651	5 to 13	11	10
Elongation, %	D638	0.6 to 1.0	300	300
Tensile modulus, psi $\times 10^{-5}$	D638	11 to 14	—	1.0
Compressive strength, psi $\times 10^{-3}$	D695	33 to 45	—	—
Flexural yield strength, psi $\times 10^{-3}$	D790	9 to 16	6.1	5.0
Impact strength, notched Izod, ft·lb/in	D256	0.2 to 0.4	2.1	3.0
Hardness, Rockwell	D785	M115 to 125	R120	R119
Flexural modulus, psi $\times 10^{-5}$	D790	—	1.75 to 4.1	1.4
Compressive modulus, psi $\times 10^{-5}$	D695	—	—	2.5
Thermal conduct., (cal/s·cm·K) $\times 10^4$	C177	6.5 to 10	5.8	5.8
Specific heat, cal/g·K	...	0.4	0.4	0.38
Linear therm. exp. coeff., K ⁻¹ $\times 10^5$	D696	4 to 4.5	8.0	8.0 to 8.3
Continuous use temperature, °C	...	99	80 to 150	80 to 120
Deflection temp., °C at 0.45 MPa	D648	43	180 to 240	150 to 185
Volume resistivity, ohm·cm	D257	0.8 to 2×10^{12}	10^{14} to 10^{15}	10^{12} to 10^{15}
Dielectric strength, kV/in	D149	270 to 300	385 to 470	440 to 510
Dielectric constant at 1 kHz	D150	7.8 to 9.2	3.9 to 4.5	4.0 to 4.9
Dissipation factor at 1 kHz	D150	0.015 to 0.036	0.02 to 0.04	0.011 to 0.06
Deleterious media	D543	Strong acids and bases	Strong acids	Strong acids
Solvents (room temperature) (Cl.H = chlorinated hydrocarbons)	...	None	Phenol and formic acid	Phenol and formic acid

*Conversion factors: 1000 psi = 6.895 MPa; 1 ft·lb/in = 53.4 J/m; 1 cal = 4.187 J; 1 kV/in = 0.0394 MV/m.

†Based on data from *Modern Plastics Encyclopedia*.

Phenol-formaldehyde (cellulose fill)	Polycarbonate	Phenoxy	Poly(phenylene oxide)	Polypropylene
1.37 to 1.46	1.2	1.17 to 1.18	1.06	0.900 to 0.910
—	1.586	1.598	—	1.49
5 to 9	9.5	8 to 9	9.6	4.5 to 6.0
0.4 to 0.8	110	50 to 100	60	100 to 600
8 to 17	3.5	3.5 to 3.9	3.55	1.6 to 2.25
25 to 31	12.5	10.4 to 12.0	16.4	5.5 to 8.0
7 to 14	13.5	12 to 13	13.5	6 to 8
0.2 to 0.6	16	1.5 to 2.0	5.0	0.4 to 1.0
E64 to 95	M70	R115 to 123	R119	R80 to 102
10 to 12	3.4	3.75 to 4.0	3.6 to 4.0	1.7 to 2.5
—	3.5	3.2 to 3.4	—	1.5 to 3.0
4 to 8	4.7	4.2	5.2	2.8
0.35 to 0.40	0.3	0.4	—	0.46
3.0 to 4.5	6.8	5.7 to 6.1	3.3 to 5.9	8.1 to 10.0
150 to 175	121	77	—	120 to 160
—	138	83 to 88	—	225 to 250
10^9 to 10^{13}	2.1×10^{16}	10^{10} to 10^{13}	10^{18}	Over 10^{16}
200 to 400	400	400 to 520	400 to 500	500 to 660
4.4 to 9.0	3.02	4.1	2.6	2.2 to 2.6
0.04 to 0.20	0.0021	0.002	0.00035	Under 0.0018
Strong bases and oxidizing acids	Bases and strong acids	Strong oxidizing acids	None	Strong oxidizing acids
None	Aromatic and Cl.H.	Aromatic and Cl.H.	Aromatic and Cl.H.	None

TABLE A5-1
Typical Properties* of Polymers Used for Molding and Extrusion† (Continued)

	ASTM test method	Polyethylene		Poly(methyl methacrylate)
		Low density	High density	
Specific gravity	D792	0.91 to 0.925	0.94 to 0.965	1.17 to 1.20
Refractive index	D542	1.51	1.54	1.49
Tensile strength, psi $\times 10^{-3}$	D638, D651	0.6 to 2.3	3.1 to 5.5	7 to 11
Elongation, %	D638	90 to 800	20 to 130	2 to 10
Tensile modulus, psi $\times 10^{-5}$	D638	0.14 to 0.38	0.6 to 1.8	3.8
Compressive strength, psi $\times 10^{-3}$	D695	—	2.7 to 3.6	12 to 18
Flexural yield strength, psi $\times 10^{-3}$	D790	—	1.0	13 to 19
Impact strength, notched Izod, ft·lb/in	D256	No break	0.5 to 20	0.3 to 0.5
Hardness, Rockwell	D785	D40 to 51 (Shore)	D60 to 70 (Shore)	M85 to 105
Flexural modulus, psi $\times 10^{-5}$	D790	0.08 to 0.6	1.0 to 2.6	4.2 to 4.6
Compressive modulus, psi $\times 10^{-5}$	D695	—	—	3.7 to 4.6
Thermal conduct., (cal/s·cm·K) $\times 10^{-4}$	C177	8.0	11 to 12	4 to 6
Specific heat, cal/g·K	...	0.55	0.55	0.35
Linear therm. exp. coeff., K ⁻¹ $\times 10^5$	D696	10 to 22	11 to 13	5 to 9
Continuous use temperature, °C	...	80 to 100	120	60 to 88
Deflection temp., °C at 0.45 MPa	D648	38 to 49	60 to 88	80 to 107
Volume resistivity, ohm·cm	D257	Over 10^{16}	Over 10^{16}	Over 10^{14}
Dielectric strength, kV/in	D149	450 to 1000	450 to 500	400
Dielectric constant at 1 kHz	D150	2.25 to 2.35	2.30 to 2.35	3.0 to 3.6
Dissipation factor at 1 kHz	D150	Under 0.0005	Under 0.0005	0.03 to 0.05
Deleterious media	D543	Oxidizing acids	Oxidizing acids	Strong bases and strong, oxidizing acids
Solvents (room temperature) (Cl.H. = chlorinated hydrocarbons)	...	None	None	Ketones, esters, aromatic and Cl.H.

* Conversion factors: 1000 psi = 6.895 MPa; 1 ft·lb/in = 53.4 J/m; 1 cal = 4.187 J; 1 kV/in = 0.0394 MV/m.

† Based on data from *Modern Plastics Encyclopedia*.

Polysulfone	Polystyrene		Poly(vinyl chloride)	
	Gen. purpose	Impact-resistant	Rigid	Plasticized
1.24	1.04 to 1.05	1.03 to 1.06	1.30 to 1.58	1.16 to 1.35
1.633	1.59 to 1.60	—	1.52 to 1.55	—
10.2 (yield)	5.3 to 7.9	3.2 to 4.9	6 to 7.5	1.5 to 3.5
50 to 100	1 to 2	13 to 50	2 to 80	200 to 450
3.6	3.5 to 4.85	2.6 to 4.65	3.5 to 6	—
13.9 (yield)	11.5 to 16	4 to 9	8 to 13	0.9 to 1.7
15.4 (yield)	8.7 to 14	5 to 12	10 to 16	—
1.2	0.25 to 0.40	0.5 to 11	0.4 to 20	—
M69, R120	M65 to 80	M20 to 80	D65 to 85 (Shore)	A40 to 100 (Shore)
3.9	4.3 to 4.7	3.3 to 4.0	3 to 5	—
3.7	—	—	—	—
2.8	2.4 to 3.3	1.0 to 3.0	3.5 to 5.0	3.0 to 4.0
0.31	0.32	0.32 to 0.35	0.2 to 0.28	0.3 to 0.5
5.2 to 5.6	6 to 8	3.4 to 21	5 to 10	7 to 25
150 to 175	66 to 77	60 to 79	65 to 80	65 to 80
180	75 to 100	75 to 95	57 to 82	—
5×10^{16}	Over 10^{16}	Over 10^{16}	Over 10^{16}	10^{11} to 10^{15}
425	500 to 700	300 to 600	425 to 1300	300 to 1000
3.13	2.4 to 2.65	2.4 to 4.5	3.0 to 3.3	4 to 8
0.001	0.0001 to 0.0003	0.0004 to 0.002	0.009 to 0.017	0.07 to 0.16
None	Strong, oxidizing acids	Strong, oxidizing acids	None	None
Aromatic hydrocarbons	Aromatic and Cl.H.	Aromatic and Cl.H.	Ketones, esters, swelling in aromatic and Cl.H.	Plasticizer may be extracted. Otherwise like rigid PVC

TABLE A5-2
Typical Properties of Representative Textile Fibers*

Fiber identification		Breaking tenacity, g/denier		Elongation at break, %	
Generic name	Chemical name	Standard	Wet	Standard	Wet
1. Rayon (viscose)	Regenerated cellulose				
<i>a.</i> Regular		0.7–3.2	0.7–1.8	15–30	20–40
<i>b.</i> High tenacity		3.0–5.7	1.9–4.3	9–26	14–34
2. Acetate	Cellulose acetate				
<i>a.</i> Diacetate		1.2–1.4	0.8–1.0	25–45	35–50
<i>b.</i> Triacetate		1.1–1.3	0.8–1.0	26–40	30–40
3. Spandex	Segmented poly-urethane	0.7–0.9	...	400–625	...
4. Fluorocarbon	Poly(tetrafluoro-ethylene)	0.9–2.0	0.9–2.0	19–140	19–140
5. Glass	(Silica, silicates)	9.6–19.9	6.7–19.9	3.1–5.3	2.2–5.3
6. Polyester	Poly(ethylene terephthalate)	2.2–9.5	2.2–9.5	12–55	12–55
7. Acrylic	Polyacrylonitrile	2.0–2.7	1.6–2.2	34–50	34–60
8. Nylon					
<i>a.</i> Nylon 6		4.0–9.0	3.7–8.2	16–50	19–47
<i>b.</i> Nylon 66		3.0–9.5	2.6–8.0	16–66	18–70
9. Aramid					
<i>a.</i> Kevlar (DuPont)		21.7	21.7	2.5–4	2.5–4
<i>b.</i> Nomex (DuPont)		4.0–5.3	3.0–4.1	22–32	20–30
10. Olefin					
<i>a.</i> Polyethylene (branched)		1.0–3.0	1.0–3.0	20–80	20–80
<i>b.</i> Polyethylene (linear)		3.5–7.0	3.5–7.0	10–45	10–45
<i>c.</i> Polypropylene		3.0–8.0	3.0–8.0	14–80	14–80
11. Cotton	α -Cellulose	3.0–4.9	3.0–5.4	3–10	
12. Wool	Protein	1.0–2.0	0.8–1.8	20–40	

*Based on information in *Textile World*, 128(8):57 (1978). Tensile strength (MPa) = tenacity (g/denier) $\times$ density (g/cm³) $\times$ 88.3.

Specific gravity	Water absorbed at 70°F, 65% rel. humidity, %	Thermal stability
1.46-1.54	11-13	<i>a.</i> Loses strength at 150°C <i>b.</i> Decomposes at 175-240°C
1.32	6.4	<i>a.</i> Sticks at 175-205°C; softens, 205-230°C; melts, 260°C
1.3	3.2	<i>b.</i> Melts at 300°C
1.21	1.3	Sticks at 215°C
2.1	Nil	Melts at about 288°C
2.49-2.55	Nil	Softens at 730-850°C; does not burn
1.38	0.4-0.8	Sticks at 230°C; melts, 250°C
1.17	1.5	Shrinks 5% at 253°C
1.14	2.8-5.0	<i>a.</i> Melts at 216°C; decomposes, 315°C
1.14	4.2-4.5	<i>b.</i> Sticks at 230°C; melts, 250-260°C
1.44	4.5-7	<i>a.</i> Decomposes at 500°C
1.38	6.5	<i>b.</i> Decomposes at 370°C
0.92	Nil	<i>a.</i> Softens at 105-115°C; melts, 110-120°C; shrinks 5% at 75°C
0.95	Nil	<i>b.</i> Softens at 115-125°C; melts, 125-138°C; shrinks 5% at 75-80°C
0.90	0.01-0.1	<i>c.</i> Softens at 140-175°C; melts, 160-177°C; shrinks 5% at 100-130°C
1.54	7-8.5	Decomposes at 150°C
1.32	11-17	Decomposes at 130°C

TABLE A 5-3
Typical Properties of Cross-Linked Rubber Compounds

a. Diene-based polymers and copolymers						
	cis-1,4-Polyisoprene (natural rubber, also made synthetically) NR (nat.);* IR (syn.)	cis-1,4-Polybutadiene BR	Styrene-butadiene random copolymer, 25 wt % styrene SBR	Styrene-butadiene block copolymer, about 25% styrene (YSBR)	Polychloroprene (neoprene) CR	Butadiene-acrylonitrile random copolymer, variable % acrylonitrile, NBR
						Reclaimed rubber (whole tires) (mainly NR and SBR)
Gum stock (cross-linked, unfilled):						
Density, g/cm ³	0.93	0.93	0.94	0.94-1.03	1.23	1.00
Tensile strength, psi	2500-3000	200-1000	200-400	1700-3700	3000-4000	500-1000
Resistivity, ohm·cm, log	15-17	...	15	13	11	10
Dielect. const. at 1 kHz	2.3-3.0	2.3-3.0	3.0	3.4	9.0	13
Diss. factor, at 1 kHz	0.002-0.003	0.002-0.003	0.003	0.01	0.03	0.055
Dielectric str., kV/in	...	...	...	485	150-600	
Reinforced stock:						
Tensile strength, psi	3000-4000	2000-3500	2000-3500	1000-3000	3000-4000	500-1000
Elong. at break, %	300-700	300-700	300-700	500-1000	300-700	300-400
Hardness, Shore A	20-100	30-100	40-100	40-85	20-100	50-100
Resilience	Excellent	Excellent	Good	Excellent	Good	Fair
Stiffening temp., °C	-30 to -45	-35 to -50	-20 to -45	-50 to -60	-10 to -30	0 to -30
Brittle temp., °C	-60	-70	-60	-70	-40 to -55	-15 to -55
Cont. high temp. limit, °C	100	100	110	65	120	100
						1.2 (compd'd)

Resistance to:

Acid	Good	Good	Good	Good	Good	Good	Good	Good	Good
Alkali	Good	Good	Good	Good	Good	Good	Good	Good	Good
Gasoline and oil	Poor	Poor	Poor	Poor	Poor	Poor	Poor	Excellent	Poor
Aromatic hydrocarbons	Poor	Poor	Poor	Poor	Poor	Poor	Poor	Good	Poor
Ketones	Good	Good	Good	Good	Good	Good	Good	Poor	Good
Chlorinated solvents	Poor	Poor	Poor	Poor	Poor	Poor	Poor	Poor	Poor
Oxidation	Good	Good	Good	Good	Good	Good	Excellent	Fair	Good
Ozone	Poor	Poor	Poor	Poor	Poor	Poor	Excellent	Poor	Poor
Gamma radiation	Good	Good	Good	Good	Good	Good	Poor	Fair	Good
Advantages	High resilience and strength; abrasion-resistant	Low heat buildup in flexing; good resilience; abrasion-resistant	Low price; good wearing; bonds easily	Easily injection-molded; not cross-linked	Flame-resistant; good resistance to oxygen, ozone, oil, and gasoline	Excellent resistance to oil and gasoline (non-swelling)	Excellent resistance to oil and gasoline (non-swelling)	Excellent resistance to oil and gasoline (non-swelling)	Low price; easy processing; good weathering
Typical applications	Tires, tubes, belts, bumpers, tubing, gaskets, seals, foamed mattresses and padding	Tire treads, mechanical goods	Tires, mechanical goods	Toys, rubber bands, mechanical goods	Gaskets, tubing, O-rings, seals, gasoline hose	Gaskets, tubing, O-rings, gasoline hose	Gaskets, tubing, O-rings, gasoline hose	Tire carcasses, battery boxes, friction tape, soles and heels	

*This abbreviation and all following are ASTM abbreviations. 1000 psi = 6.895 MPa; 1 kV/in = 0.0394 MV/m.

TABLE A5-3
Typical Properties of Cross-Linked Rubber Compounds (Continued)

b. Saturated, carbon-chain polymers									
	Polyisobutylene (Butyl rubber, copolymer with 0.5-2% isoprene) IIR	Ethylene- propylene random copolymer, 50% ethylene EPM	Ethylene- propylene random terpolymer, 50% ethylene EPDM	Chlorosulfonated polyethylene CSM	Poly(ethyl acrylate), usually a copolymer ACM	Vinylidene fluoride-chloro- trifluoro ethylene random copolymer FKM	Vinylidene fluoride-hexa- fluoro propylene random copolymer FKM		
Gum stock (cross-linked, unfilled):									
Density, g/cm ³	0.92	0.86	0.86	1.12-1.28	1.10	1.85	1.85		
Tensile str., psi*	2500-3000	500	200	2500	200-400	200-2500	2000		
Resistivity, ohm•cm, log	17	16	16	14	...	14	13		
Dielect. const., 1 kHz	2.1-2.4	3.0-3.5	3.0-3.5	7-10	...	6			
Diss. factor, at 1 kHz	0.003	0.004-0.008	0.004-0.008	0.03-0.07	...	0.05	0.03-0.04		
Dielectric str., kV/in	600	900	900	500	...	600	250-750		
Reinforced stock:									
Tensile str., psi	2000-3000	1000-3000	1000-3500	3000	1500-2500	1500-2500	1500-2500		
Total elong., %	300-700	200-300	200-300	300-500	250-350	300-400	300-400		
Hardness, Shore A	30-100	30-100	30-100	50-100	40-100	50-90	50-90		
Stiff'g. temp., °C	-25 to -45	-40	-40	-10 to -30	...	-35			
Brittle temp., °C	-60	-50 to -75	-50 to -75	-40 to -55	-30	-50	-45		
Cont. high temp. limit, °C	120	150	150	160	175	200	250		
Resilience	Fair	Good	Good	Good	Fair	Fair	Fair		

TABLE A5-3
Typical Properties of Cross-Linked Rubber Compounds (Continued)

c. Heterochain polymers							
	Poly(dimethyl siloxane) (silicone rubber), usually copolymer with vinyl groups VMQ	Poly(dimethyl siloxane) copolymer with phenyl-bearing siloxane and vinyl groups PVMQ	Room-temp. vulcanizing silicone	Polysulfide ET and EOT	Polyurethane AU and EU	Poly(epichlorohydrin) CO	Epichlorohydrin-ethylene oxide random copolymer, 32% eth. oxide ECO
Gum stock (cross-linked, unfilled):							
Density, g/cm ³	0.98	0.98	1.0-1.3 (cmpd'd)	1.35	1.25	1.36	1.27
Tensile strength, psi*	50-100	50-100	...	100-200	2000-4000	100-300	200-400
Resistivity, ohm-cm, log	11-17	11-17	15	12	11-14		
Dielect. const. at 1 kHz	3.0-3.5	3.0-3.5	2.8	7-9.5	5-8		
Diss. factor at 1 kHz	0.001-0.010	0.001-0.010	0.003	0.001-0.005	0.02-0.09		
Dielectric str., kV/in	100-600	100-600	500	250-600	350-525		
Reinforced stock:							
Tensile strength, psi	500-1200	500-1500	400-800	1300-1800	3000-10,000	1500-2500	2000-3000
Elong. at break, %	200-700	200-700	100-200	200-500	200-600	200	200
Hardness, Shore A	30-80	30-80	30-50	25-85	20-100	60-80	60-80
Resilience	Fair	Fair	Fair	Fair	Poor	Fair	Fair
Stiffening temp., °C	-50	-100	-50 to -100	-25	-25 to -35	-25	-45
Brittle temp., °C	-50	-120	-50 to -100	-50	-50 to -60		
Cont. high temp. limit, °C	250	300	200-250	120	120	150	150

Resistance to:		Fair	Fair	Fair	Fair	Fair	Fair	Fair	Good	Good
Acid		Fair	Fair	Fair	Fair	Fair	Fair	Fair	Good	Good
Alkali		Fair	Fair	Fair	Fair	Fair	Fair	Poor to fair	Good	Good
Gasoline and oil		Poor	Poor	Poor	Poor	Excellent	Excellent	Excellent	Good	Good
Aromatic hydrocarbons		Poor	Poor	Poor	Poor	Excellent	Good	Good	Fair	Fair
Ketones		Excellent	Excellent	Excellent	Excellent	Excellent	Good	Poor	Poor	Poor
Chlorinated solvents		Poor	Poor	Poor	Poor	Excellent	Good	Poor	Poor	Poor
Oxidation		Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Good
Ozone		Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
Gamma radiation		Good	Good	Good	Good	Good	Good	Good	Good	Excellent
Advantages		High temp. stability and low temp. flexibility; good electrical properties	Wire and cable insulation, tubing for aircraft systems, surgical implants			Can be cast in place; good electrical stab.	Resists swelling in gasoline and oil	Excellent abrasion resistance; high strength; low coeff. of friction	Good solvent resistance; low air permeability; good resistance to oxygen and ozone	
Typical applications						Caulking, seals, encapsulation, potting of elec. components	Gaskets, seals, diaphragms	Impellers, solid tires for fork-lift trucks, shoe heels	Seals, gaskets, wire and cable jackets, coatings	

*1000 psi = 6.895 MPa; 1 kV/in = 0.0394 MV/m.

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